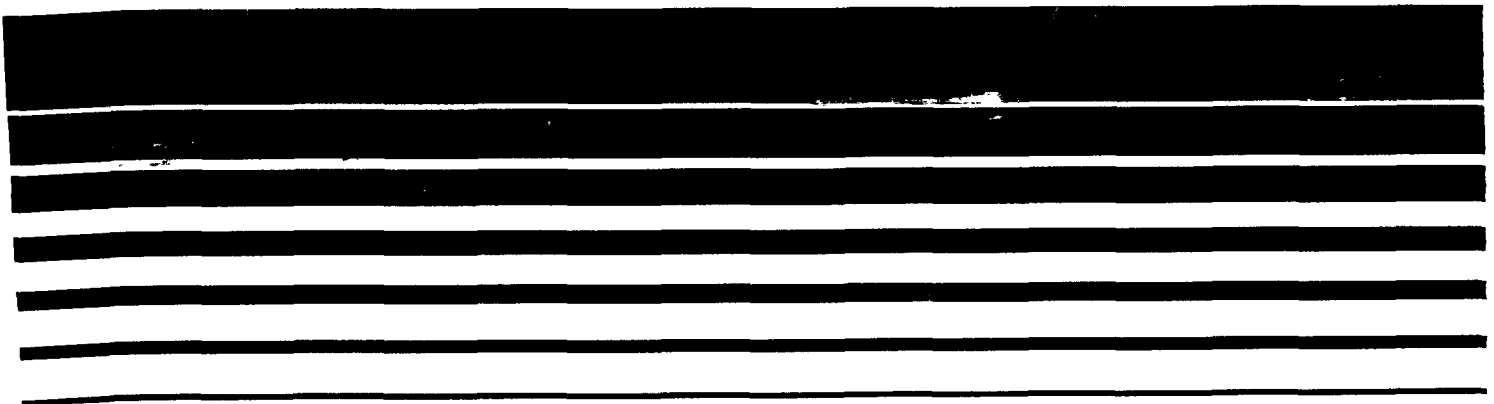




# **AIR/SUPERFUND NATIONAL TECHNICAL GUIDANCE STUDY SERIES**

## **Models for Estimating Air Emission Rates from Superfund Remedial Actions**



**EPA 451/R-93-001**

**AIR/SUPERFUND NATIONAL TECHNICAL  
GUIDANCE STUDY SERIES**

**REPORT ASF-30**

**Models for Estimating  
Air Emission Rates from  
Superfund Remedial Actions**

**U.S. Environmental Protection Agency  
Office of Air and Radiation  
Office of Air Quality Planning and Standards  
Research Triangle Park, North Carolina 27711**

**March 8, 1993**

## **DISCLAIMER**

**This report has been reviewed by the Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, and has been approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.**

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## List of Symbols

Symbol	Definition	Units
$\beta$	Bulk density	g/cm <sup>3</sup>
C	Concentration in waste/soil	ug/g
C	Concentration in water	mg/l
C <sub>g</sub>	Saturation vapor concentration	ug/m <sup>3</sup>
C <sub>l</sub>	Liquid-phase conc. in soil	g/cm <sup>3</sup>
C <sub>s</sub>	Conc. (loading) in soil	g/cm <sup>3</sup>
C <sub>v</sub>	Vapor conc. in soil pore spaces	g/cm <sup>3</sup>
μg/m <sup>3</sup>		(Section 4.1 only)
D	Phase transfer coefficient	cm <sup>2</sup> /sec
D <sub>a</sub>	Diffusivity in air	cm <sup>2</sup> /sec
D <sub>e</sub>	Effective diffusivity	cm <sup>2</sup> /sec
d <sub>e</sub>	Effective diameter	m
D <sub>w</sub>	Diffusivity in water	cm <sup>2</sup> /sec
E	Emissions	g
E <sub>a</sub>	Air-filled porosity	-
EF	Emission factor	g/VKT
ER	Emission rate	g/sec
E <sub>t</sub>	Total porosity	-
E <sub>w</sub>	Water-filled porosity	-
F	Feed rate	kg/hr
H	Henry's Law constant	atm-m <sup>3</sup> /mol
	Henry's Law constant	dimensionless (Section 4.2 only)
K	Overall mass transfer coefficient	cm/sec
k	Particle size multiplier	-
K <sub>d</sub>	Volatilization constant	1/sec
k <sub>d</sub>	Distribution coefficient	cm <sup>3</sup> /g
k <sub>G</sub>	Gas-phase mass transfer coefficient	cm/sec
k <sub>L</sub>	Liquid-phase mass transfer coefficient	cm/sec
K <sub>ow</sub>	Octanol/water partition coefficient	-
L	Flow rate	l/min
l	Depth	m
	Depth	cm (Sections 4.2 and 5.3 only)
M	Mass of waste	g
	Mass of waste	kg (Sections 4.4, 7.1, and 7.2 only)

Symbol	Definition	Units
	Volume of waste	l (Section 4.4 only)
MW	Molecular weight	g/mole
P	Vapor pressure	mm Hg
p	Days with precipitation	-
PF	Metal partitioning factor	-
p <sub>t</sub>	Erosion potential	g/m <sup>2</sup>
Q	Gas exit rate	m <sup>3</sup> /min
	Gas exit rate	m <sup>3</sup> /sec (Section 6.1 only)
Q	Soil excavation rate	m <sup>3</sup> /sec
R	Gas constant	atm-m <sup>3</sup> mmHg/mol-K (Sections 5.2 and 5.3)
	Gas constant	cm <sup>3</sup> mmHg/mole-K (Section 5.1)
	Gas constant	l-mm Hg/mole-K (Section 3.2)
r	Stoichiometric ratio	-
ρ	Density	g/cm <sup>3</sup>
S	Vehicle speed	km/hr
s	Silt fraction	-
SA	Surface area	m <sup>2</sup>
S <sub>cg</sub>	Schmidt number, gas-side	-
s <sub>L</sub>	Silt loading	g/m <sup>2</sup>
S <sub>v</sub>	Volume of soil	m <sup>3</sup>
T	Temperature	K
t	Time	sec
		days (Section 7.2 only)
U	Windspeed	m/sec
u <sub>g</sub>	Viscosity of air	g/cm-sec
V	Percent volatilized	%
V <sub>y</sub>	Velocity of gas	cm/sec
w	Number of wheels	-
W	Vehicle weight	Mg
X	Fraction emitted	-
X <sub>H<sub>2</sub>O</sub>	Percent moisture in soil	-
X <sub>i</sub>	Fraction of waste in soil	-
X <sub>mol</sub>	Mole fraction	-
X <sub>oc</sub>	Organic carbon fraction	-
Z	Enrichment factor	g metal/g soil

## **SECTION 1**

### **INTRODUCTION**

This manual is a compendium of models (equations) for estimating air emissions from Superfund sites undergoing remediation. These models predict emission rates of volatile organic compounds (VOCs) and particulate matter (PM) from both area and point sources. The following treatment processes are covered: air stripping, soil vapor extraction, thermal desorption, thermal destruction (incineration), excavation, dredging, solidification/stabilization, and bioremediation. Emission estimation methods are also presented for landfills, lagoons, and spills/leaks/open waste pits.

#### **1.1 BACKGROUND**

The U. S. Environmental Protection Agency (EPA) Air Program Office (Office of Air Quality Planning and Standards) and the Regional Air Offices have been given the responsibility and resources, beginning in 1987, to evaluate air impacts from Superfund sites and to advise Superfund Regional Offices on appropriate clean-up actions. The Air/Superfund Coordination Program was initiated to facilitate this effort and the EPA Air Program Office is responsible for its overall direction.

Assessing the air impacts of Superfund remedial actions is a significant part of the Air/Superfund Coordination program. These assessments are frequently required for planning purposes prior to actual remediation. They are, therefore, dependent on the ability to estimate emissions, rather than on site measurement approaches. Emission estimation can be complex, so the need was recognized for simple screening procedures to consistently analyze potential emissions from various remedial action alternatives.

#### **1.2 OBJECTIVE**

This report was prepared to meet the specific emission modeling needs of the Regional Offices and the Superfund Program. The objectives were to: 1) Identify emission

modeling needs of the Air/Superfund Program, 2) Select emission screening models for commonly used remedial activities, and 3) Prepare a manual which clearly demonstrates the use of these models.

### **1.3            APPROACH**

As part of the preparation for this document, the ten regional Air/Superfund Coordinators were surveyed regarding their screening model needs (as of 10/31/91). The technical material for this manual was compiled from the results of an evaluation of the existing literature; no original models are presented.

### **1.4            USES AND LIMITATIONS OF DOCUMENT**

The simple screening models contained in this compendium will not accurately predict emissions for all possible scenarios. In some cases, the existing field and process data are too incomplete to adequately assess the validity of certain model assumptions. In addition, the selection criteria for models included simplicity and ease of use in addition to accuracy. Where uncertainty exists, these models and the default inputs have been designed to err on the side of conservatism; i.e. to overpredict emissions. The models are screening tools. They should be used to answer the question whether: 1) no emission problem is likely, or 2) further evaluation of the emissions is needed.

Each section of this document contains a discussion of the assumptions and sensitivities of that section's model; these sensitivities should be understood before the model is applied. Default values have been provided for every model, in the event that field data for these values are not available. Of course, greater accuracy will be obtained if site-specific and process-specific measurements are used whenever possible. The key variable that must be obtained from site data is the concentration or total mass of the contaminant in the material to be treated.



## **SECTION 2**

### **DISCUSSION OF EMISSION ESTIMATION PROCEDURES**

This section provides general background information about the models presented in this document and their use.

#### **2.1 TYPES OF EMISSION ESTIMATION PROCEDURES**

There are many approaches that can be used to estimate emissions from remediation processes. These approaches include:

- Use of an emission model with default values;
- Extrapolation of emissions data from laboratory-scale experiments;
- Use of an emission model with site-specific and process-specific input data;
- Extrapolation of emission rate measurements made during pilot-scale operation at the site of interest;
- Emission rate measurements during full-scale operation of the process unit of interest at a similar site; and
- Emission rate measurements during full-scale operations at the site of interest.

Field measurement data are generally preferable to model estimates. The results from models such as those presented in this document should be considered to have a large degree of uncertainty unless confirmatory field measurement data are available.

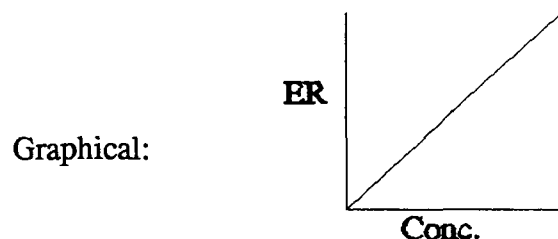
#### **2.2 GENERAL CONSIDERATIONS OF MODELS**

Various types of models are described below along with a discussion of the advantages of modeling, the limitations of modeling, and the need for calibration and validation of models.

### 2.2.1 General Types of Models

The term "model" implies a simplified or miniaturized copy of the real world. Models may be conceptual, graphical, physical, or mathematical. For example:

Conceptual: The short-term emission rate from a landfill is proportional to the concentration of the contaminant in the waste.



Mathematical:  $ER = C * k$

Physical: Pilot-scale landfill

The emission models presented in this document are all mathematical models. Mathematical models can be divided into several categories according to their underlying bases: theoretical (based on physical laws), mass balance, empirical, and heuristic. Models frequently are a mix of one or more of these types.

Theoretical models are based on fundamental physical laws. For example, an emission model for landfills may be based on Fick's 2nd Law of Diffusion, or an emission model for surface impoundments may be based on Henry's Law describing the equilibrium partitioning between the vapor and liquid concentrations of a given compound. Emission models that use a mass balance approach are based on the conservation of mass and are therefore a subset of models based on physical laws. Empirically-based models estimate emissions based on relationships or factors developed from field measurement data. In their simplest form, these types of models are emission factors, e.g. mass of emissions per unit time or unit operation. Heuristic models may be useful but can not be supported by either theory or empirical bases. This type of model is typically derived from intuition or generalized field experience. In their simplest form, heuristic models are "rules-of-thumb".

A further distinction can be made between models based on whether they describe steady-state or unsteady-state (transient) conditions. Steady state implies that under certain circumstances, variables will reach some characteristic equilibrium or constant value. For example, vapors migrating through the soil will adsorb onto soil particles or dissolve into any liquid that is present until equilibrium is achieved and all the active sites in the soil and associated liquid are saturated with the vapors. Until that point is reached, diffusion is at an unsteady state. Once all the active sites are saturated, they can typically be ignored and diffusion is considered to be at steady state conditions. In practice, most environmental problems are modeled under steady-state conditions since this greatly simplifies the number of variables to be considered and the chemical and physical processes to be modeled. In reality, however, many environmental problems exist at unsteady-state conditions, so the assumption of steady state introduces some bias.

### **2.2.2 Advantages of modeling**

The advantages of a modeling approach as opposed to other options are speed and convenience. Emission estimates can be made in a matter of minutes using a mathematical model, whereas it may take several months to obtain field measurement data. The cost differential between modeling approaches and field measurement approaches is obvious. Most importantly, emission models can be used as a planning tool to make estimates for remedial actions that have not yet taken place. In such cases, field measurement data are not an option. Models may also be useful as a predictive tool for estimating the effect of changes in waste properties or changes in operating parameters for an on-going remedial action. In such cases, if field measurement data are available for one or more set of conditions, then the accuracy of the model can be determined and empirical correction factors added if necessary.

### **2.2.3 Limitations of Models**

The estimates provided by any model are limited by the validity of the input data. For Superfund applications, this is a key concern since even fundamental information such as the types of contaminants present at the site, their concentration, and their frequency of occurrence and distribution is not usually known with much certainty. Another limitation of the models is that they usually only consider a few key variables. This simplification of reality introduces a variable amount of bias in the results. The greater the situation being modeled differs from the assumptions inherent in the model, the greater the likely bias.

Models may be misused in several ways. One, an incorrect or inappropriate model may be selected for use for a given situation. Two, incorrect input values may be used. Three, the user may fail to utilize existing site-specific or process-specific data. Four, the user may fail to recognize or consider the limitation of the model.

### **2.2.4 Calibration and Validation of Models**

Model results should be compared, whenever possible, to real-world data. Calibration of a model involves using these comparisons to adjust model parameters or to add a correction factor. Model calibration is typically either specific for a given site or for a given process, and the calibration results may not be applicable to other situations. Validation of a model involves a systematic comparison of model results to field measurements under various conditions as part of a sensitivity analysis of the model. The degree to which a given model has been validated should be determined by the model user before the data are used for any air pathway assessment.

## 2.3

### GENERAL SOURCES OF INPUT DATA

There are essentially three categories of input data for the emissions models in this document: site-specific information (e.g., contaminated area), process information (e.g., feed rate), and physical properties of contaminants (e.g., diffusivity in air). Not every model requires inputs from all three categories.

Clearly, the site-specific inputs should come from field measurements. In some cases, typical or default values are presented for cases when field measurement data are not available or are suspect. The use of default values will affect the accuracy of the emission estimates. Values for process variables should come from field observations, design documents, or vendors. Default values are presented for cases where valid data are not available, but these too will affect the accuracy of the emission estimates. Physical property data for 168 contaminants are included in Appendix A. In many cases (e.g., vapor pressure), these data are only valid for 25°C and 1 atmosphere pressure.

## **SECTION 3**

### **VOC POINT SOURCES**

Simple air emission estimation procedures are presented in this section for point sources of volatile organic compounds (VOCs), including: air strippers, soil vapor extraction systems, thermal desorption units, and thermal destruction units (incinerators). The same format is followed for each source. A brief description of the emission process is given, followed by a discussion of available air emission models. The model selected for inclusion in this manual is then presented along with sources of input data and default values for each of the input variables of the selected model. The model assumptions are then briefly discussed. Finally, an example calculation is shown and references are listed. In all cases, the models estimate uncontrolled VOC emissions.

#### **3.1 AIR STRIPPERS**

##### **3.1.1 Description of Emission Process**

Air stripping, or packed-tower air stripping, is widely used to remove chlorinated solvents and other VOCs from contaminated ground water. Air stripping is currently in use or is the proposed remedy for Superfund sites in all ten U.S. EPA regions. It is often chosen because of its cost-effectiveness and the high removal efficiencies that can be achieved.

Air stripping is a mass transfer process in which volatile contaminants are evaporated (stripped) into air. The contaminated water is introduced at the top of a packed-tower through spray nozzles and allowed to slowly flow down through the column or tower. The packing media acts to retard the water flow (increase liquid hold-up) and increase the effective surface area of the system. Air is introduced countercurrent to the direction of water flow. The saturated air containing the VOCs is emitted from the top of the column or routed to a control device. The treatment system may also contain wells, separators, and vessels for treating inorganic contaminants.

A site-specific air stripping system is typically designed and constructed for each Superfund application as opposed to using an existing design. The system design is based upon meeting a specific performance goal: e.g., some minimum percent removal of a given VOC from water at a specified flow rate. The level of uncontrolled air emissions from a given system will thus depend on the performance goal and the effectiveness of the design.

The primary source of emissions from air stripping is the stripper exhaust, and VOCs are the major pollutant of concern. For systems without control devices, the exhaust is vented through a short stack, typically a (3-6 ft) pipe, at the top of the column. For systems with control devices, the airflow from the column is usually vented down to the control device at ground level. A short stack (15-20 ft) is then used after the control device.

In addition to the exhaust stack, other emission sources may exist. Any place upstream of the air stripping tower where water is in direct contact with the atmosphere, such as separators, holding tanks, treatment tanks, or conduits, is an emission source. Fugitive losses from pumps, valves, and flanges are usually not significant due to the dilute nature of the water contamination.

The important parameters affecting the emission rate for a given compound from an air stripping unit include: the concentration of the contaminant in the influent to the stripper, the influent flowrate, the stripping efficiency of the tower, and the effectiveness of any control technologies that are in place. The stripping efficiency will depend on a number of factors including: the compound's volatility and water solubility, the type of packing material in the tower, and the gas and liquid flow rates within the tower.

### 3.1.2 Model Selection

For a given liquid treatment rate, the magnitude of the uncontrolled air emissions from an air stripper are governed by the effectiveness of the liquid-to-air mass transfer in the stripper. A number of equations and associated computer models are available to aid the system designer in selecting the appropriate tower height, gas to liquid ratio, packing material, etc. to optimize the mass transfer and meet the performance goal in a cost-effective manner<sup>1-7</sup>. These estimation procedures tend to be similar, and any of these design models could be used to predict the levels of uncontrolled air emissions. One design model for Superfund sites that is given in EPA's Air Stripper Design Manual<sup>1</sup> has been validated<sup>8</sup> by comparing the model outputs to data from multiple field sites. Air emissions are estimated from the influent mass loading and the Henry's Law constant of the compounds. This approach also served as the basis for the simple screening model developed by Eklund, et al.<sup>9</sup> that uses a mass balance approach and presents typical (default) inputs. This screening model was chosen for inclusion in this document because of its usefulness, simplicity, and connection to a field-validated model.

### 3.1.3 Emission Model Equation

A simple mass balance equation is given below for estimating the uncontrolled emission rate for VOCs from air strippers. It is assumed that all contaminants removed enter the atmosphere.

$$ER = C L (SE/100)(1.67 \times 10^{-5}) \quad (\text{Eq. 3-1})$$

where:

ER	=	emission rate of species i [g/sec];
C	=	concentration of species i in influent water [mg/L];
L	=	Influent flow rate [L/min];
SE	=	stripping efficiency [%]; and
$1.67 \times 10^{-5}$	=	conversion factor from [mg/min] to [g/sec].



### **3.1.4 Minimum Requirements for Field Data**

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of air emissions. The minimum field data required are:

- Specific contaminants present in the water to be treated;
- Average contaminant concentration in the water; and
- Maximum contaminant concentration in the water.

### **3.1.5 Sources of Input Data**

The preferred source of input data for Equation 3-1 is field measurements for the air stripping system of interest. As previously mentioned, field data should be obtained regarding the specific contaminants present in the water to be treated and their average and maximum concentration in the water. Influent water concentrations will generally be lower than the static water concentrations obtained from monitoring wells. The approximate total volume of water to be treated will be of interest to estimate the duration of the cleanup.

Values for the influent flow rate and stripping efficiency may be obtained from design specification documents and blueprints or from field measurements. Once the air stripper is in operation, a mass balance or stack sampling of emissions from the system can be performed to confirm the emission estimates. Any field measurements should be performed under steady-state conditions and during typical or average operating conditions. Worst-case, or reasonable maximum, values may also be of interest for assessing maximum, short-term air impacts.

Default values are given in the following subsection for all input variables necessary for Equation 3-1. The default values are intended to be used only if adequate site-specific and system-specific data are not available.

### 3.1.6 Default Values for Input Variables

Table 3-1 gives default values to be used in Equation 3-1 for a typical air stripper used at a Superfund site along with a default value for the gas/liquid ratio in the stripping tower. Figures 3-1 and 3-2 give a means of estimating the stripping efficiency of a compound based on its Henry's law constant and the gas/liquid (G/L) ratio. Henry's Law constants and their logs for 168 compounds are given in Appendix A. As previously discussed, the efficiency will also be a function of this G/L ratio as well as temperature, tower height, air/water contact time, and pollutant concentration. A worst-case scenario if the influent contaminant concentrations are not well known is to assume that slightly soluble organic contaminants are present in the water at their maximum solubility (see Appendix A for solubilities of some common VOCs).

If the approximate size of the air stripper is known, the values given in Table 3-2 can be used to estimate emissions using Equation 3-1. Table 3-2 also includes information regarding stack parameters to allow prediction of downwind ambient air concentrations using an EPA-approved air dispersion model.

### 3.1.7 Model Assumptions/Sensitivity Analysis

Equation 3-1 is valid under certain conditions. Most importantly, it is a steady-state equation; that is, if used to predict emissions over a period of days or weeks, it requires that the concentration of pollutant "i" in the water stays a constant, and that the stripping efficiency is also constant. To account for the change in the contaminant concentration over time, it would be necessary to monitor its concentration in the process water on a periodic basis and use these data in the emissions estimation.

Table 3-1.

**Default Values for Estimating Air Stripper Emissions**

Parameter	Symbol	Units	Default Value	Expected Range	Reference
Concentration of species i in influent water	C	mg/L	maximum water solubility of species i (see Appendix A)	--	--
Influent flow rate	L	L/min	5,700	570 - 5,700	9
Stripping Efficiency	SE	%	100	90 - 100	-- <sup>b</sup>
Gas to Liquid Ratio <sup>a</sup>	G/L	L/L	50	20 - 200	10

<sup>a</sup>For use with Figures 3-1 and 3-2.

<sup>b</sup>Expected range of design criteria for VOC removal.

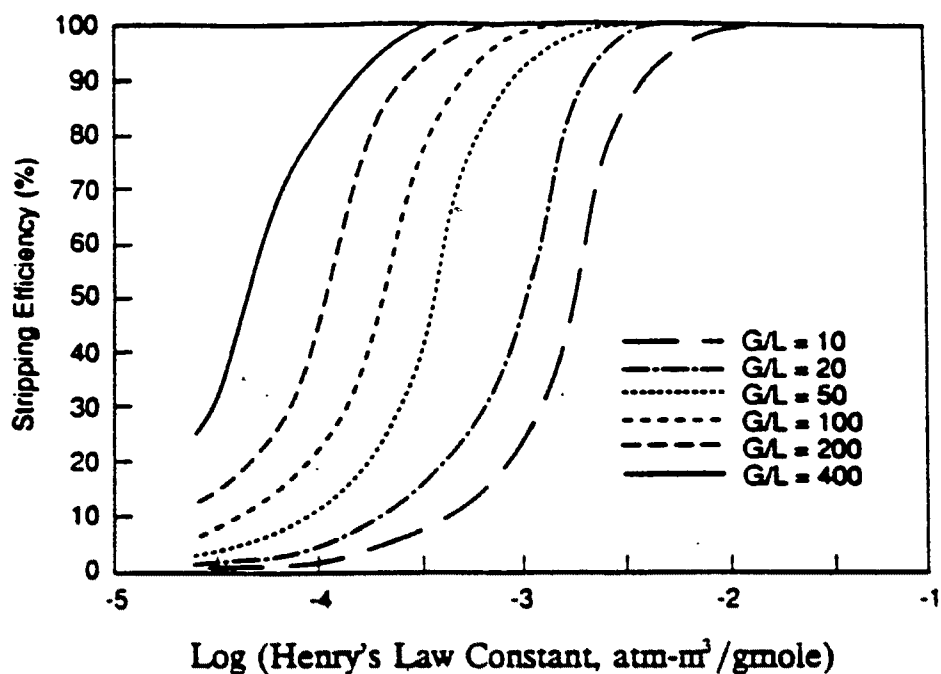


Figure 3-1. Stripper efficiency vs. Henry's Law constant, parameter =  $G/L$  (vol/vol), low efficiency range.

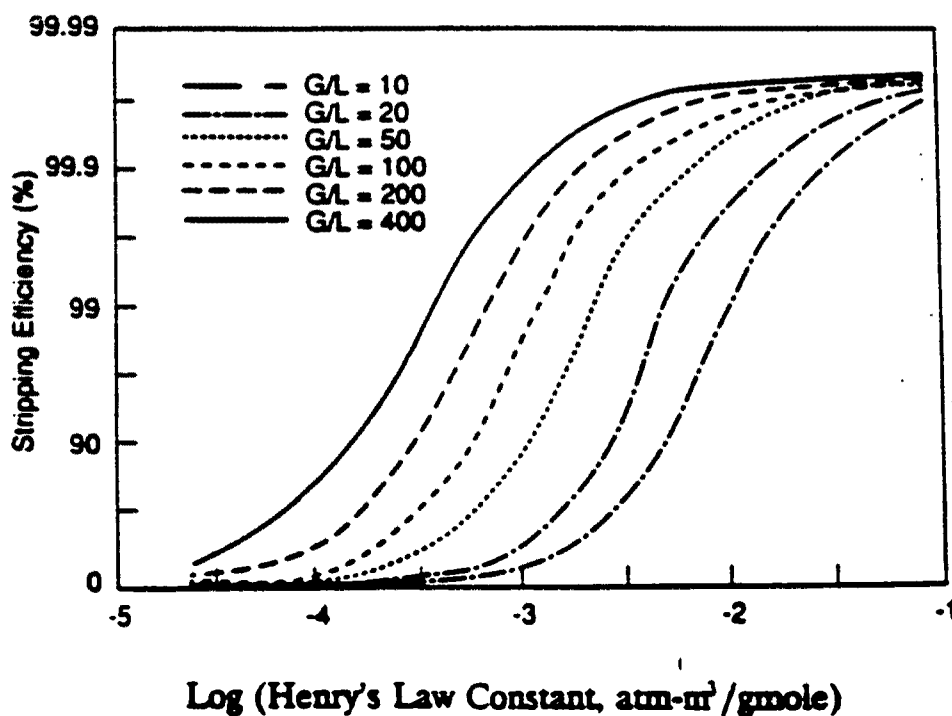


Figure 3-2. Stripper efficiency vs. Henry's Law constant, parameter =  $G/L$  (vol/vol), high efficiency range.

Source: Reference 1

**Table 3-2.**

**Example Scenarios for Air Stripping**

Parameter	Units	Typical Value		
		Small	Medium	Large
Total influent liquid flowrate	L/min	570	2,840	5,700
	gpm	150	750	1,500
Column Height	m	7.6	9	14
Column Diameter	m	1.2	3.6	3.6
Exhaust Gas Flowrate	m <sup>3</sup> /min	29	140	285
	cfm	1,020	5,000	10,000
Stack Height	m	8.5	10	15
Stack Diameter	m	0.31	0.61	0.91
Structure Dimensions	m	7.6 x 1.2 x 1.2	9.0 x 3.6 x 3.6	13.0 x 3.6 x 3.6
Exit Gas Velocity	m/sec	6.4	8.0	7.3
Exit Gas Temperature	°C	20	20	20
Ambient Temperature	°C	20	20	20
Air/Liquid Ratio (G/L)	vol/vol	50	50	50

SOURCE: Reference 9

The biggest uncertainty in estimating air stripper emissions is in the values for the contaminant concentration in the influent water. The water composition is likely to change over time due to variability in the extent and degree of subsurface contamination across the site. Before operation of the air stripping system is initiated, only a limited set of data taken from monitoring well samples will typically be available for estimating an average contaminant concentration in the influent water. Furthermore, the measurement process itself for various VOCs in water can bias the data. Substantial losses of VOCs can occur during sampling and in the first few days of sample storage. All these factors combine to increase the uncertainty in the  $C_i$  term in Equation 3-1.

A recent survey of air strippers<sup>10</sup> found that systems vary widely in their design and capacity, and that the performance between units will also vary. For a given system, the mass of VOCs stripped may vary widely over a period of several months, most likely due to changes in the composition of the water to be treated. A slight seasonal variation in performance was also found to be typical, most likely due to changes in air and water temperatures and resultant changes in the stripping efficiency. Any error in assuming a constant removal for Equation 3-1 is slight if a reasonable worst-case water concentration value is used.

### 3.1.8 Example Calculation

A contaminated aquifer to be remediated contained:

Compound	Concentration in Water (ppmw)
Trichloroethylene (TCE)	10
1,1,2-Trichloroethane (1,1,2-TCA)	20
Phenol	20

The air stripper chosen for the task had a water flow rate of 2200 gpm.

To calculate the potential emissions from this project using Equation 3-1, a stripper efficiency is needed. A conservative estimation may be reached using the default value of 100%. However, it is more accurate to calculate the efficiency of each compound using Appendix A and Figures 3-1 and 3-2. Use of these figures to estimate efficiency requires a G/L value for the stripper. Since the G/L was not specified, assume the G/L default value of 50.

From Appendix A, the logarithms of the Henry's Law constants are -3.13, -2.04, and -6.34 for 1,1,2-TCA, TCE, and phenol, respectively. Figure 3-2 then gives stripper efficiencies of about 90% for 1,1,2-TCA and 99.9% for TCE.

For phenol, Figure 3-1 indicates that the stripper efficiency would be near zero. This is because phenol is relatively hydrophilic and essentially non-volatile, and one may assume that no emissions will occur during the air stripping. If the concentration in the discharge water exceeds applicable regulations, then some other means for its control would need to be considered.

All that remains before using Equation 3-1 is the conversion of units from gpm to L/min and from ppm or ppb to g/L. Using 1 ppm = 1 mg/L for dilutely contaminated water:

$$10 \text{ ppm TCE} = 10 \text{ mg/L TCE}$$

$$20 \text{ ppm TCA} = 20 \text{ mg/L TCA}$$

Making use of the fact that 1 gal = 3.7854 L, the following emissions are found via Equation 3-1:

$$ER_{TCE} = 10 \times 2200 \times 3.7854 \times (99.9/100) \times 1.67 \times 10^{-5} = 1.4 \text{ g/sec}$$

$$ER_{TCA} = 20 \times 2200 \times 3.7854 \times (90/100) \times 1.67 \times 10^{-5} = 2.5 \text{ g/sec.}$$

### 3.1.9 References

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## **3.2 SOIL VAPOR EXTRACTION**

### **3.2.1 Description of Emission Process**

Soil vapor extraction (SVE) is frequently used for the treatment of soil contaminated with volatile hydrocarbons. The process is also referred to as soil venting, vacuum extraction, aeration, or in-situ volatilization. In general terms, soil vapor extraction removes volatile organic constituents from contaminated soil by creating sufficient subsurface air flow to strip contaminants from the vadose (unsaturated) zone by volatilization. As the contaminant vapors are removed, they may be vented directly to the atmosphere or controlled in a number of ways. Among the relative advantages of SVE over other remediation approaches is that the air emissions are released from a point source and thus can readily be controlled.

Soil vapor extraction has been widely used to remediate sites contaminated with gasoline or chlorinated solvents (e.g. TCE). It is also sometimes used to minimize migration of vapors into structures or residential areas during other types of remediation. By its nature, SVE is an on-site, in-situ treatment method. It is often used in conjunction with or following other remedial measures such as excavation of subsurface waste bodies, removal (pumping) of any hydrocarbon lens that is present, or air stripping of contaminated ground water.

Typical SVE systems include extraction wells, monitoring wells, air inlet wells, vacuum pumps, vapor treatment devices, vapor/liquid separators and liquid phase treatment devices (if contaminated water is extracted in the process). Various design and operating options may be employed such as sparging, steam/heat injection, and pulsed operation. A site-specific SVE system is typically designed and constructed for each Superfund application as opposed to using an existing design. The system design is based upon meeting a specific performance goal: e.g., some minimum rate of VOC removal. The level of uncontrolled air emissions from a given system will thus depend on the performance goal and the effectiveness of the design.

The primary source of emissions from SVE systems is the exhaust gas stack, and VOCs are the major pollutant of concern. Stack heights are typically 12-30 feet and usually only one stack is used. Additional releases of volatile organics may occur from any entrained contaminated water that is extracted with the vapor. Entrained water is typically collected in a knock-out chamber or drum. Fugitive emissions are considered negligible due to the negative pressure throughout most of the system.

The contaminants removed from the soil by SVE systems and hence present in the off-gas generally have vapor pressures greater than 1.0 mm Hg at 20° C. The tendency of the organic contaminants to partition into water or to be adsorbed onto soil particles also affects the off-gas composition, as do the compound's water solubility, Henry's Law constant, and soil sorption coefficient. The soil temperature affects each of these variables and hence the rate of vapor diffusion and transport. Bulk soil temperatures are typically constant unless steam or large volumes of heated make-up air are introduced into the soil. The concentration of contaminants that are initially present will also affect their relative partitioning between vapor and liquid phases, and the amount that is solubilized or adsorbed. The time that the contamination has been present is also an important factor, as mixtures of contaminants will generally become depleted of their more volatile components over time through volatilization. This process, referred to as weathering, will tend to cause SVE to become progressively less applicable as the site ages. It also affects the operation of the SVE system, as the more volatile components are typically removed first and the composition of the vapors collected and treated varies over time.

The emission rate of VOC compounds over time from continuously operated SVE systems tends to show an exponential-type decay curve. If the system is stopped and then restarted, however, the VOC emission rate returns to near the original rate unless the remediation is nearing completion. Apparently, shutting off the vacuum allows the soil-gas equilibrium to become re-established. Due to this behavior, the most efficient method of operation is to run the SVE system only for a part of each day or week, i.e. operate in a "pulsed" mode.

Bioventing can be considered a subset of soil vapor extraction. In bioventing, however, the goal is to provide oxygen to subsurface microorganisms and thereby optimize conditions for biodegradation rather than to physically transfer pollutants from soil pore spaces to the atmosphere. Air is withdrawn from the soil and oxygen-rich ambient air is introduced via air inlet wells. The exhaust gas from a bioventing system will be less concentrated than SVE exhaust gas, and the total flowrate may be only 10-20% of a typical vapor extraction rate for a SVE system.

### **3.2.2 Model Selection**

While attempts have been made to model SVE systems as vapor transport through a porous media<sup>1-3</sup>, the authors have generally conceded that accurate prediction is not possible due to the complex nature of subsurface vapor transport and the large variations in soil permeability to air flow across most sites. Therefore, the SVE system design is typically based on pilot-scale feasibility tests at the site or other empirical determinations of the flow rate of vapors (i.e., air permeability) through the soil<sup>1,4,5</sup>.

Various equations to assist in the design of SVE systems have been presented<sup>4</sup> and incorporated into a software package called HyperVentilate. A remediation company, VAPEX, has published similar equations<sup>6</sup> and incorporated them into their 3-D AIR™ model. For estimates from either of these models to be meaningful, however, detailed information about the air permeability of the soil at the site must be known.

A simple screening model has been developed by Eklund, et al.<sup>7</sup> based on historical vapor extraction rates at sites where SVE systems have been used. The screening model document encourages the user to provide site-specific extraction rate and vapor concentration data, but also provides conservative default values. This model was selected for inclusion in this manual (a similar screening model document is currently being prepared for bioventing).

### 3.2.3 Emission Model Equation

There are several approaches for estimating the emissions from a SVE system. The best method is to directly measure the emissions from the site during full-scale or pilot operation. This approach would not entail the use of an emission model equation. A simple check of the total emissions potential for the site may be performed using Equation 3-2, which divides the total mass of contaminants in the soil by the expected duration of the site remediation:

#### Average Emission Potential

$$ER_{AVG} = M/t = S_v C (1) \beta / t \quad (\text{Eq. 3-2})$$

where:

$ER_{AVG}$	=	average emission rate of species i [g/sec];
$M$	=	total mass of contaminant in soil [g];
$S_v$	=	volume of contaminated soil to be treated [ $m^3$ ];
$C$	=	average contaminant concentration of species i in soil [ $\mu g/g$ ];
$\beta$	=	bulk density of soil [ $g/cm^3$ ];
$1$	=	constant [ $g/10^6 \mu g \times 10^6 cm^3/m^3$ ]; and
$t$	=	duration of remediation [sec].

Because Equation 3-2 assumes a 100% recovery of VOCs at a uniform rate throughout the remediation process, it should be used only as a gross estimate of the average emission rate from the SVE system over reasonably long time periods (e.g., weeks or months). It may serve as a preliminary check of the site's emission potential if either direct field measurements or a predictive model such as Equation 3-3 are to be used.

To estimate emissions over relatively short time periods or to estimate maximum emission rates, Equation 3-3 should be used. Equation 3-3 is a mass balance model for SVE emissions that requires site-specific inputs:

### Emission Rate

$$ER = C_g (10^6) Q/60 \quad (\text{Eq. 3-3})$$

where:

ER	=	emission rate [g/sec];
$C_g$	=	concentration of pollutant in extracted vapor [ $\mu\text{g}/\text{m}^3$ ];
Q	=	vapor extraction rate [ $\text{m}^3/\text{min}$ ];
$10^6$	=	conversion factor [g/ $\mu\text{g}$ ]; and
1/60	=	conversion factor [min/sec].

If these inputs are not available, a conservative but less accurate estimation may be made using the default values given below.

#### **3.2.4 Minimum Requirements for Field Data**

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of air emissions. The minimum field data required are:

- Specific contaminants present in the soil to be treated; and
- Average contaminant concentration in the soil.

To use Equation 3-2, field data are necessary also to estimate the total volume of contaminated soil to be treated.

#### **3.2.5 Sources of Input Data**

Although provided as a very simple screening model, Equation 3-2 nonetheless requires some knowledge of site characteristics: the volume of contaminated soil to be treated,  $S_v$ , the contaminant concentration,  $C_g$ , and the duration of the remediation project,  $t$ .

Pilot-scale field tests are typically performed to assist in SVE system design. If no site data are available for the extraction rate,  $Q$ , an approximation may be made from soil-air permeability measurements, if these are available. In the absence of any field data, default values found in the next subsection may be used.

Measuring the concentrations in headspace vapors above the contaminated soil is the next best approach to estimating  $C_g$ . If these data are not available, a very conservative value may be reached with the use of Equation 3-4, which assumes the soil is saturated with the contaminant:

$$C_g = P \text{ MW } (10^9) / (R \text{ T}) \quad (\text{Eq. 3-4})$$

where:

$C_g$	=	saturated value of contaminant vapor concentration [ $\mu\text{g}/\text{m}^3$ ];
$P$	=	contaminant vapor pressure at soil temperature [mm Hg];
$\text{MW}$	=	molecular weight of contaminant [g/g-mole];
$10^9$	=	conversion factor [ $\mu\text{g-L}/\text{g-m}^3$ ];
$R$	=	ideal gas constant = 62.4 [L-mm Hg/ mole-° K]; and
$T$	=	absolute temperature of soil [° K].

Values of  $C_g$  at 25° C (298° K),  $P_{\text{vap}}$ , and MW for various VOCs may be found in Appendix A. The use of Equation 3-4 may result in a significant overestimation of the emission rate (see Section 3.2.7).

Once the SVE system is in operation, stack sampling of emissions from the system can be performed to confirm the emission estimates. The guidance given in Section 3.1.4 for field measurements of air strippers applies to all remediation technologies, including SVE systems.

### 3.2.6 Default Values for Input Variables

Table 3-3 gives default values to be used in Equation 3-3 for a typical soil vapor extraction system used at a Superfund site. A worst-case scenario if the soil-gas concentration is not known is to assume that the soil-gas is saturated with the VOC of interest as shown in the preceding subsection.

If the approximate size of the SVE system is known, the values given in Table 3-4 can be used to estimate emissions using Equation 3-3. Table 3-4 also includes information regarding stack parameters to allow prediction of downwind ambient air concentrations using an EPA-approved air dispersion model.

### **3.2.7 Model Assumptions/Sensitivity Analysis**

The largest uncertainty in estimating SVE emissions is in the values for the concentration of the pollutant in the extracted vapors. The vapor composition may change rapidly over relatively short periods of time. As previously noted, the composition and concentration of vapors will depend on whether or not the operation of the SVE system is continuous in nature or is intermittent (pulsed).

Before operation of the SVE system is initiated, only a limited set of pilot scale data will typically be available for estimating achievable extraction rates as well as for estimating soil-gas concentrations. The representativeness of this pilot-scale data will be difficult to assess until full-scale operations are underway.

As mentioned above, Equation 3-2 is intended for estimating total emissions over the course of the clean-up. It will be less accurate than Equation 3-3 for estimating short-term emission rates. This is because the former assumes a 100% removal efficiency and a constant removal rate, whereas this removal efficiency is not achieved in practice, and further, the removal rate drops over time. This drop may be less important if the operation is "pulsed", allowing soil-gas concentration to be periodically re-established at levels near that of the initial concentration.

**Table 3-3.**

**Default Values for Estimating SVE System Emissions**

Parameter	Symbol	Units	Default Value	Expected Range	Reference
Concentration of pollutant in extracted vapor	$C_g$	$\mu\text{g}/\text{m}^3$	Maximum: saturated vapor conc. (see Appendix A)	--	--
			Typical: $3 \times 10^6$	--	8
Vapor extraction rate	Q	$\text{m}^3/\text{min}$	85	1.4 - 425	7
Bulk density of soil	$\beta$	$\text{g}/\text{cm}^3$	1.5	1.0 - 2.0	9
Duration of remediation	t	sec	$1.58 \times 10^7$ (6 months)	$0.79 \times 10^7$ - $9.46 \times 10^7$	Author's estimate

\*Based on case studies of SVE that indicate that the exhaust gas concentration is typically less than 1,000 ppm per given VOC compound.

**Table 3-4.**

**Example Scenarios for SVE with No Controls Based on Size of System**

Parameter	Units	Scenario			
		Very Small	Small	Medium	Large
Exhaust gas flowrate	$\text{m}^3/\text{min}$	1.4	14	85	425
	cfm	50	500	3,000	15,000
Exhaust gas velocity	m/sec	3.0	7.4	12.5	14.2
Exit gas temperature	$^{\circ}\text{C}$	50	50	50	50
Stack height	m	3.0	4.6	7.6	9.1
Stack diameter	m	0.10	0.20	0.38	0.46

\*Assume three adjacent stacks each handling 5,000 cfm. The flow is split to lower the velocity of the exiting gas to typical design levels to minimize damage to the stack.

Source: Reference 7



It is important to note that Equation 3-4 gives the theoretical maximum value of  $C_g$ , and will significantly overpredict the concentration for any contaminants present at relatively low levels. Equation 3-4 will also overpredict the long-term average value of  $C_g$ , as the concentration of contaminants in the soil tend to decrease over time. This decrease is a function of the soil type, and in general cannot be accurately modeled, although in principle the decrease is exponential.

### 3.2.8 Example Calculation

A contaminated site to be remediated contains soil contaminated to the following extent:

Benzene:	100 ppm	(100 $\mu\text{g/g}$ )
Toluene:	300 ppm	(300 $\mu\text{g/g}$ )
Carbon Tetrachloride:	50 ppb	(0.050 $\mu\text{g/g}$ )
Naphthalene:	800 ppb	(0.800 $\mu\text{g/g}$ )

The site is a 200 m<sup>2</sup> field behind a factory. The water table is 30 m below the surface at this location. The entire volume of soil down to the water table is assumed to be contaminated. A vendor has quoted an estimate of five months to complete the clean-up. No physical data on the type of soil is known.

Using Equation 3-2, a rough estimate of the long-term average emission rate may be obtained, assuming continual operation for 150 days ( $1.3 \times 10^7$  seconds), and using the default bulk density of 1.5 g/cm<sup>3</sup>. The uncontrolled emissions are:

$$\begin{aligned} ER_{\text{benz}} &= (200 \times 30) \times (100) \times (1.5) / (1.3 \times 10^7) = 0.069 \text{ g/sec} \\ ER_{\text{tolu}} &= (200 \times 30) \times (300) \times (1.5) / (1.3 \times 10^7) = 0.21 \text{ g/sec} \\ ER_{\text{CCl}_4} &= (200 \times 30) \times (0.05) \times (1.5) / (1.3 \times 10^7) = 3.5 \times 10^{-5} \text{ g/sec} \\ ER_{\text{napt}} &= (200 \times 30) \times (0.8) \times (1.5) / (1.3 \times 10^7) = 5.5 \times 10^{-4} \text{ g/sec.} \end{aligned}$$

The short-term emission rates are calculated with Equation 3-3. Use of this equation requires knowledge of the vapor extraction rate; for this scenario, a medium-sized SVE system of 85 m<sup>3</sup>/min may be assumed. One further needs the concentration of the extracted vapors. The saturated vapor concentrations obtained from Appendix A (in ug/m<sup>3</sup>) are:

benzene	4.00 x 10 <sup>8</sup>
toluene	1.49 x 10 <sup>8</sup>
carbon tetrachloride	9.34 x 10 <sup>8</sup>
naphthalene	1.58 x 10 <sup>5</sup>

These values all assume that the soil is saturated with each contaminant. Given the low concentrations present in the soil, the extracted vapor will actually be well below saturation. This can be checked by using the partial pressure,  $P_i$  (see Equation 4-10), in place of  $P$  in Equation 3-4. Therefore, the "typical" default value for VOCs of 3x10<sup>6</sup> ug/m<sup>3</sup> for the exhaust gas concentration will be used for each compound except naphthalene (where the saturated value is actually lower since naphthalene is a semi-volatile compound rather than a VOC).

Putting these values into Equation 3-3 yields:

$$\begin{aligned} ER_{\text{benz}} &= (3 \times 10^6) \times (10^6) \times (85)/(60) = 4.2 \text{ g/sec} \\ ER_{\text{tolu}} &= (3 \times 10^6) \times (10^6) \times (85)/(60) = 4.2 \text{ g/sec} \\ ER_{\text{CCl}_4} &= (3 \times 10^6) \times (10^6) \times (85)/(60) = 4.2 \text{ g/sec} \\ ER_{\text{naph}} &= (1.58 \times 10^5) \times (10^6) \times (85)/(60) = 0.22 \text{ g/sec.} \end{aligned}$$

In this case, the two sets of emission rates vary by at least an order of magnitude. If the air pathway assessment using the higher values from Equation 3-3 indicates that the air emissions are at unacceptable levels, then better estimates of the extracted vapor concentration should be obtained via field measurements, so that more accurate emission rate estimates can be determined.

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### **3.3 THERMAL INCINERATION**

#### **3.3.1 Description of Emission Process**

Thermal incineration, also known as thermal destruction, high-temperature thermal treatment, thermal oxidation, or incineration, is a commonly proposed remedy for Superfund sites. Its primary advantage is that it results in the destruction of toxic organic compounds. Add-on control devices for VOCs are not necessary.

Several types of incinerators are now in use at Superfund sites, but rotary-kiln designs are the most common. The emission estimation methods presented in this section are valid for any design, but the default values given are only valid for rotary-kiln incinerators.

Incineration technology is primarily used for the remediation of organic compounds. The emissions of organic compounds, therefore, depend on the destruction and removal efficiency (DRE) of the incinerator. The DRE is a function of the incinerator's operating conditions (residence time, temperature, etc.) and can not be accurately predicted, but it can be determined by a trial burn or treatability test.

The emission rates for organic compounds can be estimated by assuming that the DREs exactly meet the regulated standards. For example, RCRA standards require a DRE of 99.99 percent for each principal organic hazardous constituent (POHC) in the waste. (POHCs are compounds that are chosen for the trial burn as an indication of the DRE of total hydrocarbons). Other DREs can be assumed for dioxins, PCBs, etc.

Products of incomplete combustion (PIC) are formed by the reactions of organic compounds in the intense heat of the combustion chamber. PICs such as dioxins, furans, and other polynuclear aromatic hydrocarbons (PAH) will be emitted even if not present in the waste stream. As yet, there is no known accurate method of predicting PIC emissions.

### 3.3.2 Model Selection

Models have been reported<sup>1</sup> for direct-fired high temperature rotary kiln systems that predict the temperature of the solid bed and the kiln exit gas as a function of measurable physical parameters such as kiln rotational speed, burner firing rate, soil feed rate, soil moisture content, and whether the operation is co-current or counter-current. Ho and Ding<sup>2</sup> have presented the results of a similar model (but not the equations themselves) for an oxygen combustion system. These models could be combined with thermal stability data<sup>3,4</sup> to predict the destruction efficiency of incinerators. The oxygen content of the kiln gas is also an important variable<sup>3</sup> and would need to be considered. Much work would be required before this type of model was ready for field validation.

Several computerized models are available for permit writers and incinerator operators to use in predicting the performance of incineration systems<sup>5,6</sup>. These computer programs have not been purchased or examined for this study. The marketing literature for these programs, however, implies that these models use an assumed destruction and removal efficiency (DRE) and can then be used to predict such factors as fuel requirements, gas flows, stack temperature and velocity, pressure drops, etc. These models do not appear to be appropriate for use as screening models given their cost and requirement for access to a personal computer. They also do not appear to offer improved accuracy over the simple mass balance equations discussed below.

Simple mass balance equations for estimating incineration emissions with an assumed DRE have been previously developed by Eklund, et al.<sup>7</sup>. These same general equations were slightly modified and used by IT in another EPA study to estimate the air impacts from incinerators<sup>8</sup>. Both of these documents summarize typical operating rates, control efficiencies, etc. The equations from Reference 8 meet the selection criteria and are presented in Section 3.3.3.

Air emissions from materials handling operations upstream of the incinerator should also be evaluated. Emissions from excavation and storage piles are addressed in Sections 4.1 and 5.3, respectively. No good models exist for waste mixing and waste feed operations. Whenever possible, such operations should take place in an enclosure that is vented to the incinerator or to another control device.

### 3.3.3 Emission Model Equation

Only emissions of organic compounds are addressed in this section; emissions of particulate matter and metals are covered in Section 6. Equation 3-5 provides the emission rate estimation:

$$ER = 0.278 F (1 - DRE/100) \quad (\text{Eq. 3-5})$$

where:

ER	=	emission rate of organic contaminant of interest [g/sec];
F	=	feed rate of organic contaminant of interest [kg/hr];
DRE	=	destruction and removal efficiency of organic contaminant of interest [%]; and
0.278	=	conversion factor [kg/hr] to [g/sec].

The feed rate of organic may be found using Equation 3-6:

$$F = 10^6 F_T C \quad (\text{Eq. 3-6})$$

where:

$F_T$	=	total feed rate of waste into incinerator [kg/hr];
$10^6$	=	conversion factor [g/ug]; and
C	=	concentration of the contaminant of interest [ $\mu$ g/g].

The concentration of a group of organic compounds is found by summing the concentrations of each compound within the group.

### 3.3.4 Minimum Requirements for Field Data

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of air emissions. The minimum field data required are:

- Specific contaminants present in the soil or waste to be treated;
- Average contaminant concentration in the soil or waste; and
- Maximum contaminant concentration in the soil or waste.

### **3.3.5 Sources of Input Data**

The primary source of input data for Equations 3-5 and 3-6 are field measurements and design specifications. Accurate values for the feed rate and contaminant concentration should be available from the RI/FS and from any trial burns. Otherwise, the incinerator vendors may be able to provide a typical feed rate for the system, although this will depend upon waste type.

### **3.3.6 Default Values for Input Variables**

Table 3-5 gives default values to be used in Equations 3-5 and 3-6 for a typical incineration system used on-site at a Superfund site.

If the approximate capacity of the incinerator is known, the values given in Table 3-6 can be used to estimate emissions using Equation 3-5. Table 3-6 also includes information regarding stack parameters to allow prediction of downwind ambient air concentrations using an EPA-approved air dispersion model.

### **3.3.7 Model Assumptions/Sensitivity Analysis**

Equations 3-5 and 3-6 assume a uniform feed rate and a uniform concentration of contaminant in the waste. If the waste is homogenous and if the concentrations of contaminants do not vary much, then the first assumption will be valid. However, if the concentrations do vary significantly, then the feed rate may need to be altered to maintain the same DREs, depending on the system. Generally, if the concentrations vary, then operating conditions (residence time, excess oxygen, etc.) are altered to ensure the minimum DRE standards are met.

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### 3.4 THERMAL DESORPTION

#### 3.4.1 Description of Emission Process

In the thermal desorption process, volatile and semi-volatile contaminants are removed from soils, sediments, slurries, and filter cakes. This process typically operates at temperatures of 200° -1000° F but is often referred to as low temperature thermal desorption to differentiate it from incineration. At these lower temperatures, the process promotes physical separation of the components rather than combustion.

In thermal desorption processes, contaminated soil is removed from the ground and transferred to treatment units, making this an *ex situ* process. After it is excavated, the waste material is screened to remove objects greater than 1.5" in diameter before being introduced to the desorber. In general, three desorber designs are used: an indirectly fired rotary dryer, internally heated screw augers, or a fluidized bed. The treatment systems include both mobile process units designed specifically for treating soil and asphalt kilns, which can be adapted to treat soils. Direct or indirect heat exchange vaporizes the volatile compounds producing an off-gas that is typically treated before being vented to the atmosphere.

Because thermal desorbers may operate near or above 1000° F, some pyrolysis and oxidation may occur in addition to the vaporization of water and organic compounds. Collection and control equipment such as afterburners, fabric filters, activated carbon, or condensers prevent the release of the contaminants to the atmosphere.

Thermal desorbers effectively treat soils, sludges and filter cakes and remove volatile and semi-volatile organic compounds. Some higher boiling point substances such as polychlorinated biphenyls (PCB's) and dioxins may also be removed and thus be present in the off-gas (usually associated with the particulate matter). VOC removal is enhanced if the soil contains 10-15 percent moisture prior to treatment since water vapor carries out some VOCs.

Point sources of air emissions from thermal desorption vary widely with each process. The stack of an afterburner vents combustion products, as does a fuel-fired heating system if the combustion gases are not fed into the desorber. The fuel-fired heating system typically operates with propane, natural gas or fuel oil. If controlled, the stack will vent small concentrations of the original VOC contaminants, as well as products of any chemical reactions that might occur from the control devices such as baghouse, scrubber, and vapor phase carbon adsorber. Relative to incineration, the off-gas volume to be treated from thermal desorption may be smaller, there is less likelihood of creating dioxins and other oxidation products, and metals are less likely to partition to the gas-phase. As with incineration, air emission control devices are always part of the system design (the estimates of uncontrolled emissions obtained from this manual can be used to help estimate the required removal efficiency of an emission control system or the size and cost of a given control system).

Fugitive emissions from area sources may contribute significantly to the total air emissions from a remediation site. Probably the largest source is excavation of the contaminated soil. Other sources may include the classifier, feed conveyor, and the feed hopper. Fugitive emissions from the components of the thermal desorption system and controls are possible as well. Emissions may also emanate from the waste streams such as exhaust gases from the heating system, treated soil, particulate control dust, untreated oil from the oil/water separator, spent carbon from a liquid- or vapor-phase carbon adsorber, treated water, and scrubber sludge.

### **3.4.2 Model Selection**

Thermal desorption units are currently being developed by numerous vendors. The units each have characteristic operating ranges, and typically require pilot-scale tests of the soil at a given site to find the optimum (i.e. most cost-effective) soil feedrate, residence time, and operating temperature for each application. In some cases, a tiered

evaluation involving laboratory screening, bench-scale, and pilot-scale tests may be preferable before selecting thermal desorption as a remedy for a given site<sup>1</sup>.

Theoretical models have been proposed to predict the evolution of volatile compounds from soil in a laboratory-scale indirectly heated rotary dryer system<sup>2</sup>. Particle desorption and bed desorption were examined using partial differential equations based on mass and energy balances and on the Freundlich isotherm equation. While the equations showed good agreement with experimental data, they are not readily useful for modeling other types of thermal desorption processes. In addition, the model has not been tested for full-scale systems or with a range of soil and contaminant types.

A simple screening model has been developed by Eklund, et al.<sup>3</sup> based on a mass balance approach. The only inputs to the screening model are the concentration of contaminants in the soil, the mass rate of soil being treated, and the percentage of the contaminants that are volatilized. Default or typical values for the last two terms could be developed from existing pilot-scale and full-scale test results (summarized in Reference 3) in an analogous manner to what has been done for SVE systems. This model is the only screening model identified for inclusion in this compendium.

The same considerations regarding air emissions from upstream materials handling operations that are discussed in Section 3.3.2 for thermal incineration also apply to thermal desorption systems.

### **3.4.3 Emission Model Equation**

Equation 3-7 gives a mass-balance model of uncontrolled VOC emissions from a desorption unit. This equation does not take into account emissions from excavation or materials handling; those may be found in Section 4.1. Fugitive emissions from the desorber system must be calculated on an ad hoc basis. It is assumed that no control device is present, so any combustion gases or PICs from fume incinerators would require further modeling.

(Eq. 3-7)

$$ER = \left( \frac{C}{1000} \right) \left( \frac{F_T}{3600} \right) \left( \frac{V}{100} \right)$$

where:

ER	=	emission rate for contaminant of interest i [g/sec];
C	=	concentration of the contaminant of interest [ $\mu$ g/g];
1000	=	conversion factor [g • g/ $\mu$ g • kg];
F <sub>T</sub>	=	total feed rate of waste into process unit [kg/hr];
3600	=	conversion factor [sec/hr]; and
V	=	fraction of contaminant that is volatilized [%].

Note that the units of C are  $\mu$ g/g, which is equivalent to ppmw.

#### 3.4.4 Minimum Requirements for Field Data

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of air emissions. The minimum field data required are:

- Specific contaminants present in the soil or waste to be treated;
- Average contaminant concentration in the soil or waste; and
- Maximum contaminant concentration in the soil or waste.

#### 3.4.5 Sources of Input Data

The preferred source of input data for Equation 3-7 is field measurements for the thermal desorption system of interest. As indicated above, field data should be obtained regarding the specific contaminants present in the material to be treated and their average and maximum concentration. Values for the flow rate of material to the desorber and the volatilization efficiency may be obtained from design specification documents and blueprints or from field measurements. Once the thermal desorption unit is in operation, stack sampling of emissions from the system can be performed to confirm the emission estimates.

### 3.4.6 Default Values for Input Variables

Table 3-7 gives default values to be used in Equation 3-7 for a typical thermal desorption system used at a Superfund site. Tables 3-8 and 3-9 contain information regarding stack parameters to assist in the prediction of downwind ambient air concentrations using an EPA-approved air dispersion model.

### 3.4.7 Model Assumptions/Sensitivity Analysis

The emission estimation equation assumes the waste material is fed into the process unit at a constant rate and that the material is uniformly contaminated. The former assumption is reasonable, but the waste material will certainly have a degree of variability in the contaminants present and their concentrations. The accuracy of the emission estimate can be improved if the distribution of soil contaminants in the waste material can be taken into account. For example, the site may contain several areas where the contamination in each area is consistent within an order of magnitude. The emissions associated with the clean-up of each area could be estimated separately to improve the accuracy of the overall emission estimate.

The removal efficiency (i.e., percent volatilized) or RE of the thermal desorption unit for various compounds will vary. The operating temperature and residence time of the process unit will obviously affect the RE. In addition, the moisture content of the waste material and the concentration range will also influence the fraction of a given organic contaminant that is volatilized.

### 3.4.8 Example Calculations

A site to be remediated contains soil with the following levels of contamination:

Benzene	1.0 $\mu\text{g/g}$
Toluene	24.0 $\mu\text{g/g}$
Xylene	110.0 $\mu\text{g/g}$
Ethyl Benzene	20.0 $\mu\text{g/g}$

Table 3-7.

## Default Values for Thermal Desorption Units

Parameter	Symbol	Units	Default Value	Expected Range	Reference
Feed rate	F <sub>T</sub>	kg/hr	27,200	2,700 - 90,800	3
% Volatilized	V	%	Desorber Temperature of 200-600°F	—	4
			VOCs/BTEX 99		
			SVOCs/PNAs 90		
			THC 95		
			PCBs 50		
			Desorber Temperature of 600-1000°F	—	4
			VOCs/BTEX 99.99		
			SVOCs/PNAs 99		
			THC 99.9		
			PCBs 99		
Other Parameters of Possible Interest <sup>a</sup>					
Mass of soil to be treated	Kg	--	4.5x10 <sup>5</sup> - 2.3x10 <sup>7</sup>	3	
Residence Time	min	--	3 - 70	3	

\*These parameters may be used to find the treatment rate, F, using:

$$F \left( \frac{\text{kg}}{\text{hr}} \right) = \frac{(\text{Mass of soil treated in kg}) \times 60}{(\text{Residence time in minutes})}$$

Table 3-8.

## Example Scenarios for Rotary Dryers and Asphalt Aggregate Dryers

Parameter	Units	System		
		Small	Medium	Large
Feed rate (soils)	kg/hr	7,300	27,200	59,000
Gas Volume <sup>a</sup>	m <sup>3</sup> /min	110	530	7,400
	cfm	4,000	18,700	26,000
Stack Height	m	9.1	7.6	6.1
Stack Diameter	m	0.4	1.3	1.3
Exit Gas Velocity <sup>a</sup>	m/sec	15	6.7	9.3
Exit Gas Temperature <sup>b</sup>	°C	--	--	--

<sup>a</sup>Gas volume and exit velocity assume dry standard conditions at 7% O<sub>2</sub> (20 °C, 1 atm).

<sup>b</sup>Exhaust gas temperature is highly dependent on the types of control devices used. For thermal oxidation with no off-gas cooling assume 815 °C (1500 °F). For any configuration with off-gas cooling by a heat exchanger, quench chamber, or scrubber, assume 120 °C (250 °F).

Table 3-9.

## Example Scenarios for Thermal Screws

Parameter	Units	System	
		Small	Large
Feed Rate (Soils)	kg/hr	3200	8200
Gas Volume <sup>a</sup>	m <sup>3</sup> /min	3.7	24.8
	scfm	130	875
Stack Height	m	6.7	4.6
Stack Diameter	m	0.2	0.2
Exhaust Gas Velocity	m/sec	2.0	13.2
Exhaust Gas Temperature <sup>b</sup>	°C	21	21

<sup>a</sup>Gas volume and exit velocity assume dry standard conditions at 7% O<sub>2</sub> (20 °C, 1 atm).

<sup>b</sup>Assumes off-gas treatment is condensation, which is typical for thermal screws.

The full-scale desorption unit has a capacity of 7.5 tons per hour, and the percent volatilized is 99.48 for benzene, 99.98 for the other compounds of interest.

To find the emission rate using Equation 3-7, the first thing to do is to get the input values into the proper units. The mass treatment rate of 7.5 tons/hr = 6820 kg/hr. Thus:

$$E_{\text{Benz.}} = 1.0/1000 \times 6820/3600 \times 99.48/100 = 0.0019 \text{ g/sec};$$

$$E_{\text{Tol.}} = 24/1000 \times 6820/3600 \times 99.98/100 = 0.045 \text{ g/sec};$$

$$E_{\text{Xyl.}} = 110/1000 \times 6820/3600 \times 99.98/100 = 0.21 \text{ g/sec}; \text{ and}$$

$$E_{\text{Ethyl Benz.}} = 20/1000 \times 6820/3600 \times 99.98/100 = 0.038 \text{ g/sec}.$$

### 3.4.9 References

1. Troxler, W.L., J.J. Cudahy, R. P. Zink, and S.I. Rosenthal. Thermal Desorption Guidance Document for Treating Petroleum Contaminated Soils. EPA Draft Report to James Yezzi, U.S. EPA, Edison, NJ. January 1992.
2. Lighty, J.S., G.D. Silcox, D.W. Pershing, V.A. Cundy, and D.G. Linz. Fundamentals for the Thermal Remediation of Contaminated Soils. Particle and Bed Desorption Models. ES&T Vol. 24, No. 5, pp750-757, May 1990.
3. Eklund, B., P. Thompson, A. Inglis, and W. Dulaney. Air Emissions From the Treatment of Soils Contaminated with Petroleum Fuels and Other Substances. EPA-600/R-92-124. July 1992.
4. de Percin, Paul (EPA). Personal Communication from Paul de Percin to Bart Eklund of Radian Corporation. August 1992.



## SECTION 4

### VOC AREA SOURCES

Simple air emission estimation procedures are presented in this section for area sources of volatile organic compounds (VOCs), including: excavation, dredging and dewatering, solidification/stabilization, and bioremediation. The same format is followed for each source. A brief description of the emission process is given, followed by a discussion of available air emission models. The model selected for inclusion in this manual is then presented along with sources of input data and default values for each of the input variables of the selected model. The model assumptions are then briefly discussed. Finally, an example calculation is shown and references are listed. In all cases, the models estimate uncontrolled VOC emissions.

A number of other area sources of VOC emissions may be present at Superfund sites, but no applicable estimation techniques exist. These other sources include any in-situ treatment processes (e.g., vitrification and bioremediation) and materials handling. Frequently used materials-handling procedures at hazardous waste sites that may result in VOC emissions include<sup>1</sup>: excavation and removal, dredging, pumping, size and volume reduction, separation and dewatering, conveying systems, storage containers, bulking tanks, drum handling and removal, compaction, and equipment decontamination. Only the first two items listed and dewatering are addressed in this section.

#### 4.1 EXCAVATION

##### 4.1.1 Description of Emission Process

Excavation and removal of soils contaminated with fuels is a common practice at Superfund sites. Excavation and removal may be the selected remediation approach or it may be a necessary step in a remediation approach involving treatment. If removal is the

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<sup>1</sup>U.S. EPA. Survey of Materials-Handling Technologies Used at Hazardous Waste Sites. EPA/540/2-91/010. June 1991.

preferred approach, the excavated soil is typically transported off-site for subsequent disposal at a landfill. If the soil contains large amounts of fuel or highly toxic contaminants, the soil may need to be treated off-site prior to final disposal. Excavation activities are also typically part of on-site treatment processes such as incineration, thermal desorption, batch biotreatment, landtreatment, and certain chemical and physical treatment methods. The soil is excavated and transported to the process unit and the treated soil is typically put back into place on the site.

Since it is rarely feasible or efficient to dig soil and immediately transfer the soil directly to transport vehicles or treatment systems, soil will be handled several times. In most cases, soil will be excavated and placed into a temporary holding area and then handled one to two more times on-site. Elevated levels of VOC (and PM) emissions are possible each time the soil is handled.

VOC emissions from handling operations result from the exchange of contaminant-laden soil-pore gas with the atmosphere when soil is disturbed and from diffusion of contaminants through the soil. There are multiple potential emission points for each of the various soils handling operations. For excavation, the main emission points of concern are emissions from:

- exposed waste in the excavation pit;
- material as it is dumped from the excavation bucket; and
- waste/soil in short-term storage piles.

The magnitude of VOC emissions depends on a number of factors, including the type of compounds present in the waste, the concentration and distribution of the compounds, and the porosity and moisture content of the soil. The key operational parameters are the duration and vigorousness of the handling, and the size of equipment used. The longer or more energetic the moving and handling, the greater likelihood that organic compounds will be volatilized. The equipment size influences volatilization by affecting the mean distance a volatilized molecule has to travel to reach the air/solid interface at the surface of the soil. In general, the larger the volumes of material being handled per unit operation, the lower the percentage of VOCs that are stripped from the soil. Control technologies for large area

sources such as excavation are relatively difficult to apply and are often much less effective than controls for point sources.

Relatively limited VOC emissions or emission rate data for excavation are available. The process of measuring emission rates from dynamic processes such as excavation is difficult and costly, and so has rarely been attempted. Further, the factors that govern emissions from materials handling are very complex. During excavation, for example, the physical properties of the soil that control the vapor transport rate (e.g. air-filled porosity) are changing with time and the concentration of contaminants may be rapidly decreasing.

#### **4.1.2 Model Selection**

While numerous models are available for estimating emissions from spills and buried wastes (see Section 5), little work has been done to estimate VOC emissions from dynamic processes such as materials handling. Orr<sup>1</sup> developed emission models for excavation, dumping, transportation, storage, and grading based on the RTI Landtreatment model<sup>2</sup>. The Orr model for excavation was tested in the field<sup>3</sup> and served as the basis for the development of example procedures for evaluating air impacts from soil excavation<sup>4</sup>. The model requires several iterative calculations and is therefore of limited use as a screening model. Further development of a screening model for excavation/dumping was recently completed by Eklund<sup>5</sup>.

EPA's Office of Underground Storage Tanks (OUST) has also developed a model for estimating emissions from excavation and other remediation processes<sup>6</sup>. The model is based on Fick's Law of Diffusion and can be used to calculate an emission flux from the soil-gas concentration, diffusivity in air, and air-filled porosity of the soil. The model is similar in some respects to those described above (i.e., governed by the effective diffusivity of the compound in the soil). This model, however, is essentially a simple landfill model and it is considered to be overly simplistic to accurately model excavation. The excavation/dumping model developed by Eklund is the one most suited for the scope of this document. (A more rigorous excavation model is also given in Reference 5.)

### 4.1.3 Emission Model Equation

#### Average Emission Potential

A simple check of the potential total emissions from a site undergoing remediation is given by Equation 4-1, which divides the estimated total mass of contaminants by the projected duration of activity:

$$ER = \frac{S_v C \beta 1.0}{t} \quad (\text{Eq. 4-1})$$

where:

ER	=	emission rate of compound i [g/sec];
$S_v$	=	total volume of contaminated material [ $\text{m}^3$ ];
C	=	concentration of compound i in soil [ $\mu\text{g/g}$ ];
$\beta$	=	bulk density [ $\text{g/cm}^3$ ];
1.0	=	constant [ $\text{g}/10^6\mu\text{g} \times 10^6\text{cm}^3/\text{m}^3$ ]; and
t	=	duration of remediation [sec].

Since it is assumed in this equation that all of the contaminant present in the soil will eventually volatilize, it is extremely conservative.

#### Emission Rate

The emission rate given in Equation 4-2 is the sum of emission rates from the soil pore space and from diffusion:

$$ER = ER_{PS} + ER_{DIFF} \quad (\text{Eq. 4-2})$$

$$ER_{PS} = P * Q * 0.98 \quad (\text{Eq. 4-3})$$

$$ER_{DIFF} = \frac{(C_s)(10,000)(SA)}{\left(1.22 \times 10^6 \frac{C_s}{P}\right) + \left(1.79 \times 10^9 \frac{C_s}{P}\right)^{\frac{1}{2}}} \quad (\text{Eq. 4-4})$$

where:

ER	=	total soil emission rate of compound i [g/sec];
$ER_{PS}$	=	soil porosity emission rate of i [g/sec];
$ER_{DIFF}$	=	diffusion emission rate of i [g/sec];
P	=	vapor pressure of compound i [mm Hg];
Q	=	excavation rate [ $\text{m}^3/\text{sec}$ ];
0.98	=	conversion factor [g/mm Hg - $\text{m}^3$ ];

$C_s$  = mass loading of compound i in soil [g/cm<sup>3</sup>];  
 $10,000$  = conversion factor [cm<sup>2</sup>/m<sup>2</sup>];  
 $SA$  = area of emitting surface [m<sup>2</sup>];  
 $1.22 \times 10^6$  = conversion factor [cm<sup>2</sup>-sec-mm Hg/g]; and  
 $1.79 \times 10^9$  = conversion factor [sec<sup>2</sup>-cm-mm Hg/g].

In most cases, contaminant data will be available as a soil concentration in units of ug/g (ppmw). Assuming a typical bulk density of undisturbed soil, the mass loading,  $C_s$ , can be related to the soil concentration as follows:

$$C_s = (C) (1.5 \text{ g/cm}^3)(10^{-6}) \quad (\text{Eq. 4-5})$$

where:  $C$  = Concentration of species i in soil [ug/g]; and  
 $10^{-6}$  = Conversion Factor [g/μg].

The emission rate obtained using Equation 4-3 should be compared to the total mass of contaminant present in the volume of soil excavated -  $M$ . If Equation 4-3 results in a total mass of emissions that exceeds  $\frac{1}{3}$  of  $M$ , then the following equation should be substituted for Equation 4-3:

$$ER_{ps} = M \cdot \frac{0.33}{t_{sv}} \quad (\text{Eq. 4-6})$$

where:  $t_{sv}$  = Time to excavate a given volume,  $S_v$ , of soil [sec], and

$$M = S_v \cdot 10^6 \cdot C_s \quad (\text{Eq. 4-7})$$

where:  $M$  = total mass of contaminant in soil [g]; and  
 $10^6$  = conversion factor [cm<sup>3</sup>/m<sup>3</sup>].

The emission rate obtained using Equation 4-4 will overpredict emissions if the partial pressure of the contaminant in the soil is far below the published vapor pressure of the compound. The partial pressure should be calculated as follows. The pore space concentration of the compound (assuming that all of the compound is in the vapor-phase) is:

$$C_v = \frac{(C)(\beta)(10^6)}{E_a} \quad (\text{Eq. 4-8})$$

where:  $C_v$  = concentration in soil pore spaces [ $\mu\text{g}/\text{m}^3$ ];  
 $10^6$  = conversion factor [ $\text{cm}^3/\text{m}^3$ ]; and  
 $E_a$  = air-filled porosity [dimensionless].

Assuming a typical air-filled porosity of 0.55 and a bulk density of  $1.5 \text{ g}/\text{cm}^3$ , the pore space concentration can be calculated as:

$$C_v = (C)(2.7 \times 10^6) \quad (\text{Eq. 4-9})$$

where:  $2.7 \times 10^6$  = conversion factor [ $\text{g}/\text{m}^3$ ].

The partial pressure of the contaminant can then be calculated as:

$$P_i = \frac{(C_v)(62,361)(298)(10^{-12})}{\text{MW}} \quad (\text{Eq. 4-10})$$

$$= \frac{(C_v)(1.86 \times 10^{-5})}{\text{MW}}$$

where:  $P_i$  = partial pressure of compound i [ $\text{mm Hg}$ ];  
 $62,361$  = gas constant R [ $\text{mmHg}\cdot\text{cm}^3/\text{mol}\cdot^\circ\text{K}$ ];  
 $298$  = assumed temperature [ $^\circ\text{K}$ ];  
 $10^{-12}$  = conversion factor [ $\text{g}\cdot\text{m}^3/\mu\text{g}\cdot\text{cm}^3$ ];  
 $1.86 \times 10^{-5}$  = conversion factor [ $\text{mmHg}\cdot\text{g}\cdot\text{m}^3/\text{mol}\cdot\mu\text{g}$ ]; and  
 $\text{MW}$  = molecular weight of compound i [ $\text{g}/\text{mol}$ ].

The partial pressure for a given compound obtained using Equation 4-10 should be compared to the published vapor pressure given in Appendix A. If Equation 4-10 results in a partial pressure that is below the published vapor pressure, then  $P_i$  should be substituted for  $P$  in Equation 4-4. Equation 4-4 then more closely approximates the more rigorous model is given in Reference 5.

#### 4.1.4 Minimum Requirements for Field Data

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of air emissions. The minimum field data required are:

- Specific contaminants present in the soil or waste to be excavated; and
- Average contaminant concentration in the soil or waste.

To use Equation 4-1, field data are necessary also to estimate the total volume of waste or contaminated soil to be excavated.

#### **4.1.5 Sources of Input Data**

Information regarding the contaminants present, their concentrations, the volume of soil to be excavated, and the physical properties of the soil such as bulk density will generally be developed during the RI at the site. Information regarding the excavation rate and surface area to be exposed will generally be developed during the remedial design based on data from the RI/FS.

Physical property data, including vapor pressure, are tabulated in Appendix A for 168 compounds. Data for other compounds of interest may be obtained from a chemical reference handbook (e.g., References 7 and 8).

#### **4.1.6 Default Values for Input Variables**

Table 4-1 gives default values to be used with in Equations 4-1 through 4-7 for a typical removal action at a Superfund site.

If the approximate size of the excavation job is known, the values given in Table 4-2 can be used to estimate emissions using Equation 4-2. Table 4-2 also includes information regarding the excavation to allow prediction of downwind ambient air concentrations using an EPA-approved air dispersion model.

The rate of materials handling operations at Superfund sites tend to be controlled by factors such as safety concerns, storage capacity or treatment capacity, rather than being limited by the operational capacities of the equipment that is used. For these reasons, actual materials handling rates tend to be far below typical handling rates at construction sites<sup>9</sup>.

**Table 4-1.**  
**Default Values for Emission Equations**

Parameter	Symbol	Units	Default Value	Expected Range	Reference
Vapor Pressure	P	mm Hg	see Appendix A	--	--
Volume of soil moved (per hour)	S <sub>v</sub>	m <sup>3</sup>	150	50-240	5
Excavation rate	Q	m <sup>3</sup> /sec	0.042	0.014-0.067	5
Emitting surface area	SA	m <sup>2</sup>	290	115-308	5
Total mass of contaminant <sup>a</sup>	M	g	--	--	--
Concentration in soil <sup>a</sup>	C	μg/g	--	--	--
Time to excavate a given volume of soil <sup>a</sup>	t <sub>sv</sub>	sec	--	--	--
Bulk density	β	g/cm <sup>3</sup>	1.5	1.0-2.0	10

<sup>a</sup>Obtain from RI/FS data.

**Table 4-2.**  
**Example Scenarios for Excavation of Contaminated Soil**

Parameter	Units	Scenario		
		Small	Medium	Large
Soil moved per scoop	m <sup>3</sup>	1	2	4
Number of scoops per hour	#/hr	50	75	60
Total volume of soil moved	m <sup>3</sup> /hr	50	150	240
Excavation Pit:				
Dimensions	m	10 x 5 x 1	10 x 15 x 1	10 x 12 x 2
Area	m <sup>2</sup>	50	150	120
Release height	m	0	0	0
Storage Pile:				
Dimensions	m	5 x 5 x 2	5 x 10 x 3	8 x 10 x 3
Area	m <sup>2</sup>	65	140	188
Release height	m	1	1.5	1.5

Source: Reference 5



#### 4.1.7 Model Assumptions/Sensitivity Analysis

The derivation of these equations is presented in the EPA report<sup>5</sup> along with a sensitivity analysis of the models and tabulated input parameters. A more detailed emission estimation model is also presented in that report.

The excavation equations are conservative and may tend to overpredict VOC emissions; there is insufficient field measurement data at this time to gauge the accuracy of the model.

Equation 4-1 includes the conservative assumption that all VOCs present in the material will volatilize. Furthermore, it is assumed that the emission rate will be constant and that the contaminants are evenly spread throughout the material. Equations 4-3 and 4-4 are based on the assumption that the soil pore gas is saturated with the contaminant of interest. If this is not the case, the equation may overpredict the emission rate. This is likely to be the case for contaminants present in soil at sub-ppm levels or those with relatively high vapor pressures.

#### 4.1.8 Example Calculations

A site has approximately 10,000 m<sup>3</sup> of soil contaminated with chloroform, 1,1,1-trichloroethane, and trichloroethylene in concentrations of 0.1, 10, and 1.0 ppm (μg/g), respectively. The volume of the contaminated soil is not accurately known, and neither is the excavation rate. The soil's bulk density averages 1.5 g/cm<sup>3</sup>. Removal of all contaminants is expected to take 20 days of continual operation (1.728x10<sup>6</sup> s).

First estimate the total emissions potential for the site using Equation 4-1:

$$\begin{aligned}ER_{\text{Chloro}} &= 10,000 \times 0.1 \times 1.5 \times 1 / (1.728 \times 10^6) = 8.7 \times 10^4 \text{ g/sec;} \\ER_{\text{TCE}} &= 10,000 \times 1.0 \times 1.5 \times 1 / (1.728 \times 10^6) = 8.7 \times 10^3 \text{ g/sec;} \\ER_{\text{TCA}} &= 10,000 \times 10 \times 1.5 \times 1 / (1.728 \times 10^6) = 8.7 \times 10^2 \text{ g/sec.}\end{aligned}$$

Next, compare these rates to those predicted by Equation 4-2. This requires knowledge of the excavation rate and a surface area, which may be assumed to be the default values from Table 4-1 of 0.042 m<sup>3</sup>/s and 290 m<sup>2</sup>, respectively. Also needed is the vapor pressure of the contaminant from Appendix A, which for chloroform is 208 mm Hg. Also, the concentrations must be converted from ppmw to g/cm<sup>3</sup> using Equation 4-5. The pore space emissions are estimated using Equation 4-3:

$$ER_{ps} = 208 \times 0.042 \times 0.98 = 8.6 \text{ g/sec}$$

The value,  $ER_{ps}$ , must be compared to  $\frac{1}{3} M/t_{sv}$ . The mass loading in the soil is calculated from Equation 4-5:

$$C_s = (0.1)(1.5)(10^6) = 1.5 \times 10^7$$

The amount of soil moved in one second is 0.042 m<sup>3</sup>, so after one second  $M/t_{sv}$  for chloroform would be (from Equation 4-7):

$$M/t_{sv} = 1.5 \times 10^7 \times 0.042 \times 10^6 = 6.3 \times 10^3 \text{ g/sec}$$

Since 8.6 exceeds  $(6.3 \times 10^3)/3$  then  $ER_{ps}$  is clearly greater than  $\frac{1}{3} M/t_{sv}$ . Use Equation 4-6 instead of 4-3:

$$ER_{ps} = \frac{1}{3} \times \frac{M}{t_{sv}} = \frac{\left(\frac{1}{3}\right)(6.3 \times 10^3)}{1} = 2.1 \times 10^3 \text{ g/sec}$$

From Equations 4-9 and 4-10, the partial pressure of chloroform can be calculated:

$$C_v = (0.1)(2.7 \times 10^6) = 2.7 \times 10^5 \text{ } \mu\text{g/m}^3$$

and

$$P_i = \frac{(2.7 \times 10^5)(62,361)(298)(10^{-12})}{119.38}$$

$$= 0.042 \text{ mmHg}$$

This partial pressure is below the vapor pressure value for chloroform of 208 mmHg given in Appendix A. Therefore,  $P_i$  should be substituted for  $P$  in Equation 4-4.

Next, calculate the emissions due to diffusion using Equation 4-4:

$$ER_{DIFF} = \frac{1.5 \times 10^{-7} \times 10,000 \times 290}{\frac{1.22 \times 10^6 \times 1.5 \times 10^{-7}}{0.042} + \left( \frac{1.79 \times 10^9 \times 1.5 \times 10^{-7}}{0.042} \right)^{\frac{1}{2}}} = 5.2 \times 10^{-3} \text{ g/sec}$$

The total emission rate of chloroform is thus:

$$ER = ER_{PS} + ER_{DIFF} = 0.021 + 0.0052 = 0.0262 \text{ g/sec}$$

This is somewhat greater than the  $8.7 \times 10^{-4}$  g/s rate found from Equation 4-1. Equation 4-1, however, predicts the average emission rate if all contamination in the soil were to volatilize at a constant rate. Since, excavation will not be continuously underway (i.e., 24-hours per day, seven days per week), it is reasonable that the emission rate estimate exceeds the average emission potential.

Similar calculations for  $ER_{TCE}$  and  $ER_{TCA}$  reveal that for both of these emission rates also, Equation 4-6 must be used in place of 4-3 and  $P_i$  calculated from Equation 4-10 is less than the published vapor pressure. The values found are:

$$E_{TCA} = 0.187 \text{ g/sec; and}$$

$$E_{TCE} = 0.35 \text{ g/sec.}$$

#### 4.1.9 References

1. Orr, D. Estimating VOC Emissions During Soil Handling Operations at National Priority List (NPL) Sites - Technical Note. EPA Contract No. 68-02-4392, WA54. Nov. 13, 1989.
2. U.S. EPA. Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) - Air Emission Models. EPA-450/3-87-026. November 1989.
3. Eklund, B., D. Ranum, and A. Hendler. Field Measurements of VOC Emissions from Soils Handling Operations at Superfund Sites. EPA Contract No. 68-02-4392, WA64. Sept. 14, 1990.
4. U.S. EPA. Air/Superfund National Technical Guidance Study Series - Development of Example Procedures for Evaluating the Air Impacts of Soil Excavation Associated With Superfund Remedial Actions. EPA-450/4-90-014. July 1990.
5. Eklund, B., S. Smith, and A. Hendler. Screening Procedures for Estimating Air Impacts from the Remediation of Superfund Sites. EPA-450/1-92-004. March 1992.
6. U.S. EPA. Estimating Air Emissions from Petroleum UST Cleanups. OUST. June 1989.
7. The Merck Index, 11th Ed. Merck & Co. Rahway, NJ. 1989.
8. CRC Handbook of Chemistry and Physics, 61st Edition. CRC Press. Boca Raton, Florida. 1980.
9. Church, H. Excavation Handbook. McGraw-Hill, 1981.
10. Schultz, H.L., et al. Superfund Exposure Assessment Manual. EPA/540/1-88/001. April 1988.

## **4.2 DREDGING AND DEWATERING**

### **4.2.1 Description of Emission Process**

Dredging is defined as the removal of material from the bottom of a water-covered structure or geologic formation. It may be used for removing sediments from the bottom of hazardous waste surface impoundments and the remediation of contaminated waterways. Sediment removal operations may involve hydraulic dredging or mechanical dredging. Hydraulic dredging is more commonly employed and uses hydraulic pressure differential (vacuum) to remove sediments and pump them in slurry form. The slurry usually consists of 10 to 60 percent solids. Mechanical dredging uses direct mechanical force, such as scraping, to remove sediments.

The magnitude of VOC emissions from full impoundments are dependent on the surface area of the impoundment, the depth of water, the surface area of the suspended sediment plume due to agitation, the type and amount of contamination present, the physical properties of the sediment and the associated contaminants, the length of time sediments are exposed, and the meteorological conditions. Important physical properties in the emission process are the volatility of the contaminants (i.e., their vapor pressure), and their diffusivities in air and water. Emissions from drained impoundments are dependent on the same factors listed above (with the exception of depth of water), and the air-filled porosity of the sediments also is a factor. During hydraulic dredging, bottom sediments are broken up and loose sediment particles float in the water in a plume of dilute slurry.

Sediment removal is only one step in the overall remediation process for dredging. Estimates of total VOC emissions must also consider emissions from dewatering, storage, materials handling, and treatment and/or disposal.

Dewatering is performed to increase the solids content of slurries and sludges. Processes used for dewatering include gravity separation, granular bed filters, rotary drum filters, filter presses, centrifuges, and belt filters. Emissions occur as sediments are exposed to the atmosphere during processing.

#### 4.2.2 Model Selection

Dredging models have been proposed by Thibodeaux<sup>1,2</sup> for emissions of PCBs from harbor sediments. These equations are relatively complex and require calculation of parameters such as air-side transport coefficients and Schmidt numbers. Radian is currently developing somewhat simpler dredging models for the U.S. EPA<sup>3</sup>. These are modified versions of the LAND7 model<sup>4</sup> and are considered to be more appropriate for inclusion in this manual since they involve more straightforward calculations. The applicability of this model for dredged materials depends on accounting for the high moisture content of the dredged sediments.

A dewatering model<sup>5</sup> has been developed by RTI based on field measurements of air emissions from sludge dewatering operations in the petroleum industry.

#### 4.2.3 Emission Model Equation

##### Emission Rate for Dredging

Equation 4-11 is used for the calculation of the fraction of contaminants that are emitted for an agitated sediment with no biodegradation:

$$X = 0.72 (K_d t)^{1/2} \quad (\text{Eq. 4-11})$$

where:

X	=	fraction of pollutant that is emitted [unitless];
0.72	=	empirical constant [unitless];
K <sub>d</sub>	=	contaminant volatilization constant [1/sec]; and
t	=	time sediment is exposed [sec].

In order for Equation 4-11 to be valid, the following relationship must hold:

$$\frac{H D_e t}{l^2} < 0.25 \quad (\text{Eq. 4-12})$$

where:  $H$  = Henry's Law constant [conc./conc.];  
 $D_e$  = effective diffusivity of contaminant in sediment air pores [ $\text{cm}^2/\text{sec}$ ];  
 $l$  = depth of sediment [cm].

The pollution volatilization constant,  $K_d$ , term in Equation 4-11 is determined as follows:

$$K_d = \frac{H D_e \pi^2}{4 l^2} \quad (\text{Eq. 4-13})$$

where:  $\pi$  = pi, 3.14159 [unitless].

The effective diffusivity,  $D_e$ , in Equation 4-13 is estimated as follows (a simplified version is given in Equation 4-16):

$$D_e = \frac{k_{eq} D_a \left[ \frac{E_a^{10/3}}{E_T^2} \right] + D_w \left[ \frac{E_w^{10/3}}{E_T^2} \right]}{(\rho_{sed})(k_d) + E_w + E_a k_{eq}} \quad (\text{Eq. 4-14})$$

where:  $D_a$  = diffusivity of compound in air [ $\text{cm}^2/\text{sec}$ ];  
 $E_a$  = air-filled porosity of sediment [unitless];  
 $E_T$  = total porosity of sediment [unitless];  
 $D_w$  = diffusivity of contaminant in water [ $\text{cm}^2/\text{sec}$ ];  
 $E_w$  = volumetric water content [ $E_T - E_a$ ], [unitless];  
 $\rho_{sed}$  = sediment/water bulk density [ $\text{g}/\text{cm}^3$ ]; and  
 $k_d$  = distribution coefficient [ $\text{cm}^3/\text{g}$ ].

The equilibrium coefficient between liquid and air,  $k_{eq}$ , is equal to  $H$  for dilute solutions. The distribution coefficient,  $k_d$ , can be estimated as:

$$k_d = (0.63) X_{oc} K_{ow} \quad (\text{Eq. 4-15})$$

where:  $X_{oc}$  = weight fraction of organic carbon in the sediment [dimensionless];  
 $K_{ow}$  = octanol-water partition coefficient [ $\text{cm}^3$  water/ $\text{cm}^3$  octanol];  
and  
0.63 = Empirical constant [ $\text{cm}^3/\text{g}$ ].

Using the default values given later in this section, Equation 4-14 can be simplified to:

$$D_e = \frac{0.45 D_w}{0.55 + 0.30 K_{ow}} \quad (\text{Eq. 4-16})$$

#### **Emission Rate for Dewatering**

The fraction of contaminants that are emitted over the short-term from dewatering operations can be estimated as:

$$X = \frac{(0.0068)(P)^{0.95}}{1 + [(0.0068)(P)^{0.95}]} \quad (\text{Eq. 4-17})$$

where:      X      =      fraction of pollutant that is emitted [unitless]; and  
              P      =      vapor pressure of pollutant [mm Hg].

#### **4.2.4 Minimum Requirements for Field Data**

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of air emissions. The only field data required is knowledge of the specific contaminants present in the soil or waste to be dredged or dewatered.

To convert the fraction emitted into an emission rate, it is necessary to know the total mass of contaminant present. This would require field data to determine the average contaminant concentration in the soil or waste and the total volume of waste or contaminated soil to be handled.

#### **4.2.5 Sources of Input Data**

Appendix A contains Henry's Law coefficients and diffusivities of selected substances in air. The Henry's Law coefficient values from Appendix A must be converted to dimensionless units; i.e., divide by  $R \cdot T$  as shown in Section 4.2.7. Appendix A also contains values for the log of the octanol-water partition coefficient. The antilog of these values should be used in Equation 4-15, as shown in Section 4.2.7.



#### **4.2.6 Default Values for Input Variables**

Table 4-3 gives default values to be used in the emission estimation equations for a typical dredging operation. Table 4-4 also includes information regarding typical operating rates for various dredging scenarios.

For purposes of dispersion modeling, the dredging area and any storage pile that is present can be assumed to have combined dimensions of 10 m by 10 m and a release height of 1 m. Site-specific values should be used if available.

#### **4.2.7 Model Assumptions/Sensitivity Analysis**

The model is limited by the diffusion of the organic contaminant through both the air and water that fill the pore spaces of the sediment. Equations 4-11, etc. are not appropriate for undisturbed sediment or for sediment which is not exposed to air (although they will provide a conservative estimate of atmospheric emissions in this last case). The model assumes that Henry's Law applies; i.e., the solution is relatively dilute. If this is not a valid assumption, then the Henry's Law constant term would need to be replaced with a term based on Raoult's Law.

These models assume there are no emissions from the liquid surface of the impoundments. This is because dredging will not usually agitate the liquid surface to a great enough extent to significantly increase the baseline emissions of the uncontaminated water. Emissions from a stagnant surface are assumed to be negligible in comparison to emissions from dredged sludge.

The sediments are assumed to be uniformly contaminated. Water evaporation is assumed to be small, density changes due to volatilization of contaminants are expected to be negligible, and the concentration of the contaminants in air is neglected. These simplifications allow a readily usable emissions equation, so if any are incorrect, the validity of the model will become more questionable.

**Table 4-3.**  
**Default Values for Estimating Dredging Emissions**

Parameter	Symbol	Units	Default Value	Comments
Time that sediment is exposed	t	sec	--	
Depth of sediment	l	cm	100	Author's estimate
Henry's Law Constant	H	dimensionless	see Appendix A	
Diffusivity in air	D <sub>a</sub>	cm <sup>2</sup> /sec	see Appendix A	
Diffusivity in water	D <sub>w</sub>	cm <sup>2</sup> /sec	see Appendix A	
Air-filled porosity	E <sub>a</sub>	dimensionless	0	
Total porosity of sediment	E <sub>T</sub>	dimensionless	0.55 0.50	hydraulic dredge mechanical dredge
Bulk density	ρ <sub>sed</sub>	g/cm <sup>3</sup>	1.05 1.10	hydraulic dredge mechanical dredge
Octanol-water partition coefficient	K <sub>ow</sub>	dimensionless	see Appendix A	
Weight fraction of organic carbon	X <sub>oc</sub>	dimensionless	0.45	

SOURCE: Reference 3, except for depth of sediment

**Table 4-4A.**  
**Specifications and Operating Characteristics for Hydraulic Dredges**

Type	Width (ft)	Length (ft)	Dredging Depth (ft)		Reach (ft)	Solids Concentration in Dredged Material (%)	Production Rate (yd <sup>3</sup> /hr)
			Minimum	Maximum			
Cutterhead	10-12	25-60	3	20	No limit	10-20	30-60
Suction	10-12	25-60	3	20	No limit	10-15	30-60
Dustpan	10-12	25-60	3	20	No limit	10-20	30-60
Mudcat	8-9	25-40	1	15	No limit	10-60	20-150

**Table 4-4B.**  
**Specifications and Operating Characteristics for Mechanical Dredges**

Type	Bucket Capacity (yd <sup>3</sup> )	Dredging Depth (ft)		Reach (ft)	Solids Concentration in Dredged Material (%)	Production Rate (yd <sup>3</sup> /hr)
		Minimum	Maximum			
Clamshell	½	0	150	100	Up to 100	20
	1	0	150	100		35
Backhoe	1	0	22	100	Up to 100	75
	1½	0	25	100		100
	2	0	30	100		130
	3	0	45	100		203
Dragline	½	0	60	68	Up to 100	30
	¾	0	60	68		35
	1½	0	60	68		65
	3	0	60	68		113

SOURCE: Reference 3

#### 4.2.8 Example Calculations

A dredging operation is being performed to remediate a lagoon bed with sludge contaminated with carbon tetrachloride ( $\text{CCl}_4$ ). The lagoon was drained prior to the start of remediation. The dredging will remove 0.90 m of material from the bottom of the lagoon and will take 4 days ( $3.46 \times 10^5$  sec) to complete. To estimate emissions, all five of the equations in this section are used. Input values are obtained from three different sources: field data, Appendix A to this report, and the default values in Table 4-3.

The Henry's Law constant of  $\text{CCl}_4$ , from Appendix A, is  $H = 3.00 \times 10^2$  atm-m<sup>3</sup>/g-mol. To convert this to the dimensionless units required, divide by  $R \cdot T$ , the gas constant times the temperature:

$$H = \frac{(3.00 \cdot 10^{-2})}{(8.205 \cdot 10^{-5} \cdot 298)} = 1.227$$

The diffusivity in air and in water of  $\text{CCl}_4$ , from Appendix A, are  $D_a = 0.0632$  cm<sup>2</sup>/sec and  $D_w = 8.8 \times 10^{-6}$  cm<sup>2</sup>/sec. The log of the octanol-water partition coefficient is  $\log K_{ow} = 2.83$ .

The default values will be used for the other required input parameters:  $E_a = 0$  and  $X_{oc} = 0.45$ . The type of dredge has not been specified, so the more conservative values of the mechanical dredge will be used:  $E_T = 0.50$ , and  $\rho_{sed} = 1.1$  g/cm<sup>3</sup>.

Using Equation 4-15:

$$k_d = 0.63 \cdot 0.45 \cdot 10^{2.83} = 191.67.$$

This value of  $k_d$  can then be used in Equation 4-14:

$$D_e = \frac{1.227 \cdot 0.0632 \left[ \frac{0^{\frac{10}{3}}}{(.5)^2} \right] + 8.8 \times 10^{-6} \left[ \frac{(.5-0)^{\frac{10}{3}}}{(.5)^2} \right]}{1.10 \times 191.67 + (0.5-0) + 0 \cdot 1.227}$$

$$= 1.65 \times 10^{-8} \text{ cm}^2/\text{sec}$$

This value of  $D_e$  can then be used in Equation 4-12 to verify that Equation 4-11 may be used:

$$\frac{(1.227)(1.65 \times 10^{-8})(3.46 \times 10^{-5})}{(90)^2} = 8.65 \times 10^{-7}$$

This value is less than 0.25, which means that the time of exposure is in the regime where Equation 4-11 is valid.

The final step before calculating the emission fraction is the calculation of Equation 4-13:

$$K_d = \frac{1.227 \cdot 1.65 \times 10^{-8} \cdot (3.14159)^2}{(4 \cdot (90)^2)} = 6.17 \times 10^{-12}$$

The fraction of pollutant emitted can then be calculated from Equation 4-8:

$$F = 0.72 * (6.17 \times 10^{-12} \cdot 3.46 \times 10^5)^{1/2} = 1.05 \times 10^{-3} \text{ or } 0.1\%$$

The emissions estimate would be higher if a non-zero value for the air-filled porosity were used.

The emissions due to dewatering are estimated from Equation 4-17 and the vapor pressure value of 113 mm Hg for carbon tetrachloride from Appendix A:

$$X = \frac{(0.0068)(113)^{0.95}}{1 + [(0.0068)(113)^{0.95}]} = 0.378 \text{ or } 38\%$$

The emissions from dewatering greatly exceed those from dredging.

#### **4.2.9 References**

1. Thibodeaux, L.J. Modeling of VOC Emissions From Dredging at Massachusetts Site. Report to Army COE. 1989.
2. Thibodeaux, L.J. Theoretical Chemodynamic Models For Predicting Volatile Emissions To Air From Dredged Material Disposal. In: Intermedia Pollutant Transport, Edited by Allen, Cohen, and Kaplan. Plenum Publishing Corp., 1989.
3. Radian Corp. Preliminary Assessment of Potential Organic Emissions From Dredging Operations. Draft Report to Mr. Dennis Timberlake, U.S. EPA/ORD. September 30, 1991.
4. U.S. EPA. Hazardous Waste Treatment, Storage, and Disposal Facilities (TSDF) - Air Emission Models. EPA-450/3-87-026. November 1989.

### **4.3 SOLIDIFICATION/STABILIZATION**

#### **4.3.1 Description of Emission Process**

Several types of stabilization/solidification (S/S) technologies exist as alternatives for remedial action. The goal of these processes is to immobilize the toxic and hazardous constituents in the waste, usually contaminated soil or sludge. A few of these processes involve in-situ treatment, however, most generally require excavation and other soil handling activities. Nearly all the commercially available stabilization and solidification technologies are proprietary. S/S processes may be considered to be point sources of VOC emissions if the process is enclosed or has an air collection system.

Solidification and stabilization processes are usually batch operations, but may be continuous and all follow the same basic steps. Wastes are first loaded into the mix bin (wastes are sometimes dried before addition to the bin), and other materials for the solidification or stabilization are added. The contents of the bin are then thoroughly mixed. After a sufficient residence time, the treated waste is removed from the bin.

The amount of fixative added may be equal to the mass of the contaminated material. The solidified material is usually formed into blocks and allowed to cure for up to several days. The blocks can then be placed in lined excavations on-site. This description does not apply, however, to in-situ treatment methods, which use a variety of techniques (from applied high voltage to injection of stabilizing agents) to immobilize the contaminated waste in-place without excavation or soils handling.

Typical raw materials used in stabilization processes include fly ash, portland cement, cement kiln dust, lime kiln dust, or hydrated lime. Other additives that may be used to solidify or encapsulate wastes include asphalt, paraffin, polyethylene, or polypropylene.

The primary source of air emissions from stabilization and solidification processes is volatilization of organic contaminants in the waste. Volatilization can occur during waste handling activities such as soil excavation and transport or during the process of mixing the binding agents with the waste. Also, some evaporative emissions will occur from waste even after stabilization, especially during the curing period immediately after the blocks are formed. Lab studies, though, have shown that the largest fraction of volatile loss occurs during the mixing phase because heat may be required to assist mixing or generated by exothermic stabilization reactions.

In general, VOC emissions from stabilization and solidification processes will depend on the type and concentration of the VOCs in the waste, the duration and thoroughness of the mixing, the amount of heat generated in the process, and the average batch size processed. The longer or more energetic the mixing and processing, the greater likelihood that organic compounds will volatilize. The volatile losses will also increase as the temperature of the waste/binder mixture increases. Binding agents with high lime contents generally cause highly exothermic reactions. The batch size influences volatilization by affecting the mean distance a volatilized molecule has to travel to reach the air/solid interface at the surface of the stabilized waste. The larger the block of material, the lower the rate of volatilization.

During the solidification/stabilization soil remediation process, there are numerous possible VOC (and PM) emission sources. There are fugitive emissions before treatment, emissions during excavation and soil handling, during the preparation of the mixing agent, during the treatment of the contaminated soil, and, finally, emissions from the treated soil after remediation. Factors influencing the (uncontrolled) emission rate will therefore include the soil permeability before and after remediation, the exact treatment process and how the mixing is accomplished, and the composition of the mixing agent. Indeed, the latter may be specifically designed to control one certain class of contaminants, and may not be effective on any others. The impermeability of the treated soil will also determine the amount of emissions (and leachate) that escape.

#### **4.3.2 Model Selection**

Little information exists about the fate of volatile contaminants in wastes treated by stabilization and solidification methods. A literature search found no available field data on air emissions at Superfund sites using this type of remediation technology. Laboratory studies, however, have estimated that 70-90% of the volatile contaminants in the treated waste eventually evaporate. Experiments also show that most of the loss occurs within 60 minutes of mixing the waste with binding agents. The only air emissions model for solidification/stabilization is the simple mass balance equation presented by Thompson, et al.<sup>1</sup>.

#### **4.3.3 Emission Model Equation**

VOC emissions from stabilization and solidification processes can be estimated using a mass-balance approach. The following equation is applicable to ex-situ solidification/stabilization processes:

$$ER = C F (2.78 \times 10^7)(V/100) \quad (\text{Eq. 4-18})$$

where:      ER      =      emission rate of contaminant i [g/sec];  
                  C      =      concentration of contaminant i in soil [ $\mu$ g/g];  
                  F      =      treatment (feed) rate of soil [kg/hr];  
                   $2.78 \times 10^7$  =      conversion factor [g/kg • g/ $\mu$ g • hr/sec]; and  
                  V      =      fraction of contaminant i volatilized [%].

#### 4.3.4 Minimum Requirements for Field Data

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of air emissions. The only field data required is knowledge of the specific contaminants present in the soil or waste to be stabilized or solidified and the average contaminant concentration.

#### 4.3.5 Sources of Input Data

The inputs to Equation 4-18 are process- and site-specific. The treatment rate of the unit can be obtained from the vendor or estimated from design documents and the results of any feasibility study. The fraction of VOCs that will be stripped during the process will be highly dependent on the system design and operating procedures. Field test data should be obtained to estimate this parameter. The concentration of contaminant in the soil or sludge to be treated should be available from remedial investigation studies.

#### 4.3.6 Default Values for Input Variables

Table 4-5 gives default values to be used in Equation 4-18. Feed rates vary widely; values of 5 to 130 tons/hr have been published for ex-situ processes and 25 to 100 tons/hr for in-situ processes.



**Table 4-5**

**Default Values for Estimating Emissions From Solidification/Stabilization**

Parameter	Symbol	Units	Default Value	Expected Range	Reference
Feedrate	F	kg/hr	45,000	4,500-120,000 (ex-situ)	6
				23,000-91,000 (in-situ)	7
% Volatilized	V	%	80 <sup>a</sup>	40-100 <sup>a</sup>	5
			100 <sup>b</sup>	100 <sup>b</sup>	5

<sup>a</sup>During mixing

<sup>b</sup>After 40 days of curing

For purposes of dispersion modeling, an ex-situ S/S unit can be assumed to have dimensions of 5m by 5m and a release height of 2m. This is based on a 10,000 gallon tank set at ground level without any air emission collection hood, control devices, or stack. An in-situ process can be assumed to have a treatment area of 10m by 10m with a release height of 1m. For either type of process, no plume buoyancy should be assumed (even though exothermic processes may result in plumes with some rise). As always, site-specific or process-specific values should be used if available.

#### **4.3.7 Model Assumptions/Sensitivity Analysis**

The major limitation of this model is the lack of air emissions data available for developing default values for the term in the model for the percent of VOCs lost from the process. Only one field study<sup>2</sup> and two laboratory studies<sup>3,4,5</sup> of air emissions from these processes have been identified, though a third study<sup>6</sup> does provide some useful performance data. These studies show that from 40 to 100% of the VOCs present in the waste are lost during the mixing step of the processes. Essentially all of the VOCs are lost to the atmosphere by the end of the curing step.

#### **4.3.8 Example Calculations**

Assume that S/S is to be used to clean up a site that is primarily contaminated with heavy metals, but where benzene is also present in the soil at an average concentration of 0.25 ug/g (ppmw). An ex-situ process unit will be used and a treatment rate of 100 tons per hour is planned.

Using Equation 4-18 and the default value for the fraction of the benzene that will be volatilized, the emissions can be estimated once the treatment rate has been converted into the proper units. A rate of 100 tons/hr equals about 91,000 kg/hr. The estimated emissions are:

$$ER = (0.25)(91,000)(2.78 \times 10^7)(80/100) = 0.005 \text{ g/sec}$$

#### 4.3.9 References

1. Thompson, P., A. Inglis, and B. Eklund. Emission Factors For Superfund Remediation Technologies - Draft Technical Note. EPA-450/1-91-001. March 1991.
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## **4.4 BIOREMEDIATION**

### **4.4.1 Description of Emission Process**

Bioremediation of soil at Superfund sites may be either in-situ or ex-situ. Ex-situ biodegradation is the general term for treatment processes where soil or waste is excavated prior to treatment. In some cases, an aqueous slurry is created by combining soil or sludge with water and then biodegraded in a self-contained reactor or in a lined lagoon. This is an emerging technology and is often referred to as slurry biodegradation. Ideally, the waste is decomposed into carbon dioxide and water. Ex-situ bioremediation also may be performed as a "dry" process such as composting or landtreatment (e.g., use of white rot fungus).

In-situ treatment employs the natural microbiological activity of soil to decompose organic constituents. This natural biological activity may be enhanced by the use of injection wells to provide an oxygen source (such as air, pure oxygen, or hydrogen peroxide) to stimulate aerobic degradation or the addition of nutrients to support the growth of waste-consuming microorganisms. In some cases, microorganisms that have the ability to metabolize specific contaminants of interest may be added to the soil. One specific type of in-situ bioremediation process - bioventing - is discussed briefly in Section 3.2.

In-situ bioremediation at Superfund sites may also involve sequential isolation and treatment of waste areas using processes that closely resemble ex-situ processes except that it may not be necessary to excavate, pump, or otherwise transfer the waste material prior to treatment. Ex-situ processes are more developed and demonstrated than in-situ processes at this time.

Ex-situ aqueous treatment systems have a number of components, all of which could be emission sources: mix tank, bioreactor system (continuously stirred tank reactor or CSTR), or lined lagoon. Since aerobic treatment is the most common mode of operation for slurry biodegradation, aeration must be provided to the bioreactors by either floating or submerged aerators or by compressors or spargers. Other typical system components are a separation/dewatering system, a clarifier for gravity separation, and wastewater storage tanks. The soils handling steps required to deliver the contaminated soil to the treatment unit may also emit significant amounts of VOCs (and PM).

Biodegradation is actually only one of several competing mechanisms in biotreatment. For ex-situ processes, the contaminants may also be volatilized, undergo chemical degradation, or be adsorbed onto the soil particles. For in-situ processes, the same pathways exist along with leaching. The overall removal achieved by biotreatment processes represents the combined impact of all of these mechanisms. Volatilization may account for the disappearance of the majority of VOCs being treated.

In open lagoons, the primary environmental factors that influence air emissions are process temperature and wind speed. Emissions tend to increase with an increase in surface turbulence due to wind or mechanical agitation. Temperature affects emissions through its influence on microbial growth. At temperatures outside the band for optimal microbial activity, volatilization will increase. Emissions from self-contained reactors are also determined by reactor design parameters such as the amount of air or oxygen used to aerate the slurry. Higher gas flow will strip more volatiles out of solution and increase air emissions.

#### **4.4.2 Model Selection**

Many models have been proposed over the years to estimate the fate of contaminants from bioremediation processes that include an examination of volatilization and stripping fate mechanisms. Models have been compiled for activated sludge, surface impoundments, batch reactors, fixed film systems, landtreatment, in-situ soil bioremediation, etc. and the models' ability to estimate air emissions have been evaluated<sup>1</sup>. In addition, the U.S. EPA has published models for estimating air emissions from RCRA facilities such as wastewater treatment and landtreatment systems<sup>2</sup>. References 1 and 2 should be used for modeling air emissions from such conventional bioremediation processes. For in-situ processes, existing air emissions models for landtreatment could be used as a worst-case scenario; i.e., contaminated soil in direct contact with the atmosphere.

Many novel bioremediation processes have been proposed for use at Superfund sites<sup>3</sup> and air emission models for these processes have not been developed. The air emissions model considered to be best-suited for bioremediation of contaminated soil is the simple mass balance equation presented by Thompson, et al.<sup>4</sup>. The major limitation of this approach is the lack of air emissions data available for developing default values for the term in the model that accounts for the fraction of VOCs lost to the atmosphere. In addition to the Thompson model, a component of the Namkung-Rittman model<sup>1</sup> is presented for biotreatment of liquids or slurries with subsurface aeration resulting in off-gassing.

#### **4.4.3 Emission Model Equation**

The mass balance approach shown below can be used for estimating emissions from a flow-through impoundment treating contaminated water or from an ex-situ bioslurry process:

(Eq. 4-19)

$$ER = \left( \frac{\ell}{60} \right) \left( \frac{C}{1000} \right) \left( \frac{V}{100} \right)$$

where: ER = emission rate of contaminant i [g/sec];  
 $\ell$  = volume rate of water treated [L/min];  
 60 = conversion factor [sec/min];  
 C = concentration of contaminant in slurry [mg/L];  
 1000 = conversion factor [mg/g]; and  
 V = percentage of contaminant i volatilized [%].

For batch biotreatment systems such as disposal impoundments, portable covered reactors, or landfarms, Equation 4-20 may be used to estimate air emissions:

(Eq. 4-20)

$$ER = \left( \frac{M}{t} \right) \left( \frac{C}{1000} \right) \left( \frac{V}{100} \right)$$

where: ER = emission rate of contaminant i [g/sec];  
 M = mass of soil treated [Kg], or volume of water [L];  
 t = residence time in treatment system [sec];  
 C = concentration of contaminant in soil [ug/g], or liquid [mg/L];  
 1000 = conversion factor [Kg-ug/g<sup>2</sup>] for soil, or [mg/g] for liquid; and  
 V = percentage of contaminant i volatilized [%].

Note that Equation 4-20 applies to contaminants in liquid or soil, with the appropriate units chosen for mass treated and contaminant concentration.

For aqueous systems with off-gassing, the stripping rate can be estimated as follows:

(Eq. 4-21)

$$ER = \frac{Q H C 1.0}{RT}$$

where: ER = Emission rate [g/sec];  
 Q = off-gas rate [m<sup>3</sup>/min];  
 H = Henry's Law constant [atm-m<sup>3</sup>/mole];  
 C = concentration of contaminant in water [mg/L];  
 R = gas constant [8.206 x 10<sup>5</sup> m<sup>3</sup>-atm/°K-mole];  
 T = absolute temperature [°K]; and  
 1.0 = conversion factor [g/mg • 1/m<sup>3</sup>].

#### **4.4.4 Minimum Requirements for Field Data**

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of air emissions. The minimum field data required are:

- Specific contaminants present in the solid or liquid waste to be treated;
- Average contaminant concentration in the slurry, solid, or soil; and
- Percentage of contaminant volatilized from the process.

#### **4.4.5 Sources of Input Data**

The inputs to Equations 4-19, 4-20, and 4-21 are all process- and site-specific. The treatment rate or capacity of the biodegradation process unit and any off-gas rate can be obtained from the vendor or estimated from design documents and the results of any feasibility study. The fraction of VOCs that will be stripped during the process will be highly dependent on the system design and operating procedures. Field test data should be obtained to estimate this parameter. The concentration of contaminant in the soil, sludge, or water to be treated should be available from remedial investigation studies.

#### **4.4.6 Default Values for Input Variables**

The percentage of each contaminant which is volatilized in either the continuous or batch-treatment methods will vary greatly depending on the physical properties of the contaminant, the impoundment geometry, and the biological activity. Emission factors have been published for biodegradation based on theoretical studies<sup>4</sup>. For mechanically-aerated, flow-through impoundments, an assumed value of  $V$  is 80%. Field measurement data for wastewater treatment systems is summarized in Table 4-6.

The other variables are process specific; no default values are available. For purposes of dispersion modeling, the biodegradation unit can be assumed to have



**Table 4-6.**  
**Default Values for Estimating Emissions from Bioremediation**

Parameter	Symbol	Units	Default Value	Expected Range	Reference
% Volatilized	V	%	80 ( $H = 10^3$ )	--	4
			10 ( $H = 10^5$ )		
				0.2 - 21 <sup>b</sup>	5
				11 - 97 <sup>b</sup>	6
				2 - 73 <sup>c</sup>	7
				1 - 81 <sup>b</sup>	8

<sup>a</sup>For a given system, the percent volatilized should vary with the Henry's Law constant for the compounds of interest.

<sup>b</sup>Industrial wastewater treatment system

<sup>c</sup>Bench-scale reactor

H = Henry's Law Constant in atm-m<sup>3</sup>/mol.

dimensions of 5m by 5m and a release height of 2m. This is based on a 10,000 gallon tank set at ground level without any air emission collection hood, control devices, or stack. As always, site-specific or process-specific values should be used if available.

#### **4.4.7 Model Assumptions/Sensitivity Analysis**

The key variable/assumption in the emission equations is the fraction of a given VOC that is lost to the atmosphere before it is degraded. Little information exists on volatile losses from slurry biodegradation processes. Slurry processes have only recently become commercially available and field experience to date is limited. However, data on air emissions from wastewater biotreatment processes are available. The percentage of each contaminant that is volatilized will vary greatly depending on the physical properties of the contaminant and the design of the treatment system. As shown in Table 4-6, the range of values for the percent volatilized may vary over a very wide range. Due to the lack of data, a conservative assumption of 80% volatile losses was made; field measurement data should be obtained to get more accurate information for specific processes. Percentage emissions for systems without mechanical aeration would be lower.

#### **4.4.8 Example Calculations**

Consider a site with a contaminated lagoon. The lagoon holds 500,000 L with an area of 100 m<sup>2</sup>. The sludge beneath it is contaminated to a depth of about 3 m. The contaminants present in the sediments are benzene and chlorobenzene. The overlying water is considered to be uncontaminated. The concentrations are 10 ug/g benzene and 20 ug/g chlorobenzene in the sludge. The bulk density of the sediments was measured and is 2.0 g/cm<sup>3</sup>. Therefore, the 300 m<sup>3</sup> of contaminated sludge would weigh 600,000 Kg. A batch biotreatment system will be used with a treatment rate of 2000 Kg batches treated for one day (86,400 sec). The Henry's Law constants for both compounds are in the 10<sup>3</sup> range, so V is assumed to be 80%.

Using Equation 4-20 and the default value for V, the emission rates are estimated to be:

$$\begin{aligned}ER_{\text{BENZ}} &= (2,000/86,400) (10/1000) (80/100) = 1.9 \times 10^4 \text{ g/sec; and} \\ER_{\text{CHL}} &= (2,000/86,400) (20/1000) (80/100) = 3.7 \times 10^4 \text{ g/sec.}\end{aligned}$$

#### 4.4.9 References

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## SECTION 5

### NON-PROCESS VOC AREA SOURCES

This section presents simple estimation procedures for landfills, lagoons, and spill sites. Spill sites are defined to mean any site where there has been a spill or leak or where there is an open (uncovered) waste pit. Each of the estimation procedures in this section are based on those contained in EPA's Superfund Exposure Assessment Manual.

#### 5.1 COVERED LANDFILLS

##### 5.1.1 Description of Emission Process

###### Covered Landfills Without Internal Gas Generation

For the purposes of this manual, a covered landfill is a site where hazardous waste lies beneath a layer of soil. If the waste was deposited intentionally, a pit may have been excavated prior to placement of the waste. In most cases, the pit will have some type of liner such as concrete, compacted clay, or polymer sheeting. The landfill may also result from migration of contaminated groundwater, or an accidental spill or leak. In any case, the waste enters the atmosphere after it volatilizes and diffuses through the soil cover.

The VOC emission rate from subsurface contamination covered by clean soil is controlled by the rate at which gas diffuses through the soil pore spaces. Any factors that significantly affect this diffusion rate will significantly affect VOC emission rates. Important chemical processes are the adsorption of gas molecules onto the liquid film surrounding soil particles and subsequent reactions of the adsorbed molecules. The physical transport of vapors through porous media such as soil has been discussed elsewhere<sup>1-4</sup>. In general, physical transport is controlled by the diffusivity in air for the specific compound of interest and the number and type of the air spaces that are present. Macrospace due to cracks, fissures, spaces between buried drums, etc. will allow for relatively rapid mass transport. The diffusion rate through soil lacking such obvious pathways will be a function of the air-filled porosity (i.e., permeability to air). The permeability of soil to air will vary by up to

three orders of magnitude across a typical residential lot<sup>5</sup>. The air-filled porosity will also vary over time. For example, precipitation causes water to fill some of the interstitial spaces in the soil and thereby prevents diffusion from occurring.

The landfill may or may not have a cover in addition to a soil layer. Any polymer cover will inhibit emissions, but this effect will be diminished if the cover contains holes or if it has degraded over time and has become more gas permeable. The surface soils may also act as a barrier to emissions. The operation of heavy equipment at a site may lead to compaction of the soil and diminished emissions due to the change in soil porosity. Landfill surfaces, however, frequently have fissures as the result of the type of soil cover and settling of the waste over time. The fissures may be long and deep enough to extend into the waste body. Such fissures may account for a significant amount of the total emissions.

#### Covered Landfills With Internal Gas Generation

Landfills that contain municipal or sanitary wastes in addition to hazardous waste are called co-disposal sites. The municipal or sanitary wastes have a high organic content and their degradation may result in the production of large volumes of methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>) and hydrogen (H<sub>2</sub>). The gas generation results in a pressure-gradient in the soil and transport via advection of these gases through the landfill. The methane, etc. will act as a carrier gas and will enhance emissions of other VOCs. The effect of landfill gas generation is sufficiently large that vapor diffusion can be ignored.

The key variable affecting VOC emissions from co-disposal sites is the gas generation rate. This in turn is dependent on the volume of municipal wastes present, the length of time it has been in the landfill, and the levels of water, oxygen, and other nutrients in the landfill.

### 5.1.2 Model Selection

The Superfund program has previously selected simple screening models in the Superfund Exposure Assessment Manual (SEAMs)<sup>6</sup>. The landfill models from this reference were adapted for this report. The model for landfills without internal gas generation is Farmer's equation<sup>7</sup> as modified by Shen<sup>8</sup> and Farino, et al.<sup>9</sup> The literature on VOC emissions from landfills is very extensive, and recent summaries are available<sup>2,10</sup>.

### 5.1.3 Emission Model Equation

Emissions from covered landfills with no internal gas generation are described in Equation 5-1:

$$ER = \frac{D_a C_g E_a^{\frac{4}{3}} X_{mol} SA 10^{-12}}{0.01 \cdot 1} \quad (\text{Eq. 5-1})$$

where:

ER	=	emission rate of compound i [g/sec];
$D_a$	=	diffusivity of compound in air [cm <sup>2</sup> /sec];
$C_g$	=	saturation vapor concentration of compound i [μg/m <sup>3</sup> ];
SA	=	exposed area [m <sup>2</sup> ];
$E_a$	=	air-filled soil porosity [unitless];
$X_{mol}$	=	mole fraction of compound i in the waste [mol/mol];
$10^{-12}$	=	conversion factor [g/cm <sup>3</sup> / μg/m <sup>3</sup> ];
0.01	=	conversion factor [m/cm]; and
1	=	depth of soil cover [m].

The saturation vapor concentration term,  $C_g$ , may be obtained from Appendix A for many compounds of interest or calculated as follows:

$$C_g = \frac{P \cdot MW \cdot 10^{12}}{(R \cdot T)} \quad (\text{Eq. 5-2})$$

where:

P	=	vapor pressure of compound i [mm Hg];
MW	=	molecular weight of compound i [g/mol];
$10^{12}$	=	conversion factor [μg/g * cm <sup>3</sup> /m <sup>3</sup> ];
R	=	ideal gas constant 62,361 [mm Hg-cm <sup>3</sup> /mol-°K]; and
T	=	absolute temperature [°K].

The mole fraction term,  $X_{\text{mol}}$ , may be calculated as follows:

$$X_{\text{mol}} = \frac{C \text{ MW}_w}{C_w \text{ MW}} \quad (\text{Eq. 5-3})$$

where:  $C$  = concentration of compound  $i$  in soil [ $\mu\text{g/g}$ ];  
 $C_w$  = concentration of waste in soil [ $\mu\text{g/g}$ ]; and  
 $\text{MW}_w$  = molecular weight of waste [ $\text{g/mol}$ ].

The air-filled soil porosity,  $E_a$ , can be calculated as follows:

$$E_a = 1 - \left[ \frac{\beta + (\beta)(X_{\text{H}_2\text{O}})}{\rho} \right] \quad (\text{Eq. 5-4})$$

where:  $\beta$  = bulk density of soil [ $\text{g/cm}^3$ ];  
 $X_{\text{H}_2\text{O}}$  = moisture fraction in soil [wt. % moisture/100]; and  
 $\rho$  = particle density of soil [ $\text{g/cm}^3$ ].

If there is internal gas generation in a covered landfill, the following equation should be used:

$$\text{ER} = C_v \cdot V_y \cdot \text{SA} \cdot 10^4 \quad (\text{Eq. 5-5})$$

where:  $\text{ER}$  = emission rate of compound  $i$  [ $\text{g/sec}$ ];  
 $C_v$  = vapor concentration of compound  $i$  in soil pore spaces [ $\text{g/cm}^3$ ];  
 $V_y$  = mean landfill gas velocity in the soil pore spaces [ $\text{cm/sec}$ ];  
 $\text{SA}$  = exposed area [ $\text{m}^2$ ]; and  
 $10^4$  = conversion factor [ $\text{cm}^2/\text{m}^2$ ].

#### 5.1.4 Minimum Requirements for Field Data

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of air emissions. The minimum field data required to estimate emissions from landfills without internal gas generation are:

- Surface area of emitting area;
- Specific contaminants present in the landfill soil or waste;
- Average contaminant concentration in the soil or waste; and
- Average total contaminant concentration in the soil or waste.

The latter information is necessary to estimate the molecular weight of the waste term,  $MW_w$ .

For landfills with internal gas generation, the minimum field data that are required are:

- Surface area of emitting area;
- Specific contaminants present in the landfill soil-gas; and
- Average contaminant concentration in the landfill soil-gas.

### 5.1.5 Sources of Input Data

Certain inputs to Equations 5-1, 5-3, 5-4, and 5-5 should be obtained from field measurements. The vapor concentration in the soil pore spaces should be measured in the field or assumed to be saturated (assume  $C_v = C_g \times 10^{-12}$ ). Appendix A contains values for 168 compounds for the saturation vapor concentration, vapor pressure, and diffusivity in air. A simple method for estimating the diffusivity in air of a compound given the diffusion coefficient of a compound of similar molecular weight and diffusion volume is:

$$D_a = D'_a \left( \frac{MW'}{MW_i} \right)^{\frac{1}{2}} \quad (\text{Eq. 5-6})$$

where:  $D'_a$  = diffusivity in air of compound of similar volume and wt. [ $\text{cm}^2/\text{s}$ ];  
 $MW'$  = molecular weight of similar compound [ $\text{g/mol}$ ]; and  
 $MW$  = molecular weight of contaminant [ $\text{g/mol}$ ].

### 5.1.6 Default Values for Input Variables

Table 5-1 contains default values needed for estimating landfill emissions. For purposes of dispersion modeling, the 5 acre default landfill can be assumed to have dimensions of 140m by 140m and a release height of 1m.



### 5.1.7 Model Assumptions/Sensitivity Analysis

The landfill models incorporate a number of assumptions, including that the landfills are isothermal, contain no fissures or macropores, and that waste is homogeneously distributed. The model for landfills without internal gas generation, equation 5-1, is highly sensitive to the air-filled porosity of the soil cover or cap as well as the depth of the cover. The accuracy of the model for landfills with internal gas generation, equation 5-5, will depend on the validity of the input values for the soil vapor concentration and the landfill gas velocity. These parameters are difficult to measure accurately in the field.

It is not recommended that temperatures other than 298 °K (25°C) be used in equation 5-2, unless the vapor pressure term is also adjusted for temperature. Equation 5-6 is only valid for estimating a compound's diffusion coefficient from another one with a similar molecular diffusion volume and molecular weight.

### 5.1.8 Example Calculations

As an illustration of these models, consider a disposal pit known to contain 1,1-dichloroethane (DCA) and vinyl chloride. Soil core samples taken in and around the pit were analyzed and found to contain the following levels ( $\mu\text{g/g}$ ) of contaminants:

Core	1,1-DCA	Vinyl Chloride
1	900	500
2	1100	900
3	1000	800

The surface area of the pit is about 250 m<sup>2</sup>. The core samples were taken ten to twenty feet below the surface, but the cover thickness has not been measured. The total contamination in the soil is about 1% or 10,000  $\mu\text{g/g}$ . The soil porosity and density are unknown.

Table 5-1.

Default Values for Estimating VOC Emission From Landfills

Parameter	Symbol	Units	Default Value	Expected Range	Reference
Diffusivity in air	$D_a$	$\text{cm}^2/\text{sec}$	See Appendix A	—	—
Saturated vapor concentration	$C_s$	$\mu\text{g}/\text{m}^3$	See Appendix A	—	—
Surface Area	SA	$\text{m}^2$	20,000 (5 acres)	4050 - 40,500	Author's estimate
Air-filled porosity	$E_a$	unitless	0.55 (Dry, uncompacted soil) 0.35 (wet or compacted soil) 0.05 (sludges)		6
Depth of soil cover	$l$	m	1	1-5	Author's estimate
Vapor concentration in soil pore spaces	$C_v$	$\text{g}/\text{cm}^3$	$C_s \times 10^{12}$	—	—
Landfill gas velocity	$V_g$	$\text{cm}/\text{sec}$	0.00163	—	6
Vapor pressure	P	mm Hg	See Appendix A	—	6
Molecular weight of compound	MW	$\text{g}/\text{mol}$	See Appendix A	—	—
Temperature	T	$^{\circ}\text{K}$	298	278 - 328	Author's estimate
Molecular weight of waste	$\text{MW}_w$	$\text{g}/\text{mol}$	250	—	Author's estimate
Bulk density of soil	$\beta$	$\text{g}/\text{cm}^3$	1.5	1.0 - 2.0	6
Particle density of soil	$\rho$	$\text{g}/\text{cm}^3$	2.65	2.4 - 2.8	9

Due to the lack of exact information, default values will be used. The pit is therefore assumed to have a cover depth of 1 m. The site is not known to contain any municipal or sanitary wastes, so the landfill model without internal gas generation is applicable (calculations using the model with gas generation are also shown for illustrative purposes). The soil density is assumed to be 1.5 g/cm<sup>3</sup>, the molecular weight of the waste is 250 g/mol, and the porosity is 0.55.

From Appendix A, the following values are obtained:

Parameter	Units	1,1-Dichloroethane	Vinyl Chloride
Diffusivity in Air	cm <sup>2</sup> /sec	0.0919	0.0900
Saturated Vapor Conc.	g/cm <sup>3</sup>	1.24x10 <sup>9</sup>	8.94x10 <sup>9</sup>
Molecular Weight	g/mole	99	62.5

The core samples show remarkable homogeneity, and an average may be used. For 1,1-DCA the average is 1000 µg/g and for vinyl chloride it is 730 µg/g. The mole fraction of the compounds of interest in the waste is calculated using Equation 5-3:

$$X_{\text{DCA}} = \frac{(1000 \text{ } \mu\text{g/g})(250 \text{ g/mol})}{(10,000 \text{ } \mu\text{g/g})(99 \text{ g/mol})} = 0.25$$

$$X_{\text{VCL}} = \frac{(730 \text{ } \mu\text{g/g})(250 \text{ g/mol})}{(10,000 \text{ } \mu\text{g/g})(62.5 \text{ g/mol})} = 0.29$$

The emission rates can now be found from Equation 5-1:

$$\text{ER (1,1-DCA)} = \frac{(0.0919)(1.24 \cdot 10^9)(0.55)^{\frac{4}{3}}(0.25)(250)(10^{-12})}{0.01 \cdot 1} = 0.32 \text{ g/sec; and}$$

$$\text{ER(vinyl chloride)} = \frac{(0.0900)(8.94 \cdot 10^9)(0.55)^{\frac{4}{3}}(0.29)(250)(10^{-12})}{0.01 \cdot 1} = 2.5 \text{ g/sec}$$

To calculate the emission rates from 5-5 for the case of internal gas generation, one uses the saturated vapor concentrations and the default value for landfill gas velocity. The emission rates are:

$$\begin{aligned} \text{ER (1,1-DCA)} &= (1.24 \times 10^9)(10^{-12})(0.00163)(250)(10^4) = 5.1 \text{ g/sec; and} \\ \text{ER (vinyl chloride)} &= (8.94 \times 10^9)(10^{-12})(0.00163)(250)(10^4) = 36 \text{ g/sec.} \end{aligned}$$

What if headspace or soil-gas information is available, but there are no corresponding soil concentration data? The following example illustrates how to calculate emissions for a covered landfill with no internal gas generation.

A series of soil-gas samples were collected and found to contain an average benzene concentration of  $150,000 \text{ ug/m}^3$  (i.e., about 50 ppm). From Appendix A, the diffusivity in air of benzene is  $0.0932 \text{ cm}^2/\text{sec}$  and its molecular weight is 78.12. The soil-gas concentration is well below the saturated vapor concentration for benzene of  $4.00 \times 10^8 \text{ ug/m}^3$ . For other variables, the same default values apply as in the example calculations given above.

The mole fraction of benzene cannot be directly calculated from Equation 5-3 since the concentration of benzene in the soil is not known. One possible approach is to calculate the total mass of benzene present in the pore spaces and convert this to a concentration in the soil. For  $1 \text{ m}^3$  of soil with an air-filled porosity of 0.55, the following mass of benzene would be present:

$$M_{\text{Benz}} = (1 \text{ m}^3)(0.55)(150,000 \text{ ug/m}^3) = 82,500 \text{ ug}$$

Given a bulk density of  $1.5 \text{ g/cm}^3$ , the weight of  $1 \text{ m}^3$  of soil is:

$$M_{\text{Soil}} = (1 \text{ m}^3)(1.5 \text{ g/cm}^3)(10^6 \text{ cm}^3/\text{m}^3) = 1.5 \times 10^6 \text{ g}$$

The concentration of benzene in the soil can be estimated as:

$$C = M_{\text{Benz}}/M_{\text{Soil}} = 82,500 \text{ ug}/1.5 \times 10^6 \text{ g} = 0.055 \text{ ug/g}$$

The mole fraction can now be calculated using Equation 5-3:

$$X_{\text{Benz}} = (0.055 \text{ ug/g})(250 \text{ g/mol})/(10,000 \text{ ug/g})(78.12) = 1.76 \times 10^{-5}$$

The emission rate can now be found from Equation 5-1 using the average measured soil-gas concentration in place of  $C_g$ :

$$\text{ER}(\text{Benzene}) = (0.0932)(150,000)(0.55)^{4/3}(1.76 \times 10^{-5})(250)(10^{12})/(0.01)(1) = 2.8 \times 10^9 \text{ g/sec}$$

The emissions of benzene are negligible. This is reasonable since benzene is present at levels well below saturation in the soil pore spaces and, therefore, the concentration gradient (i.e., driving force) is relatively low.

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## 5.2 LAGOONS

### 5.2.1 Description of Emission Process

The rate of VOC emissions from quiescent liquid surfaces will depend on the distribution of the organic species between gas and liquid phases (Henry's Law), the concentration of the organic species in each phase, and the mass transfer characteristics (coefficients) of the species. The overall mass transfer coefficient is the most important term in controlling VOC emissions. The term consists of a resistance to mass transfer in liquid ( $k_l$ ) and a resistance to mass transfer in gas ( $k_g$ ). For most VOCs  $k_g \gg k_l$  and the liquid phase resistance controls the volatilization process. For mass transfer, the chemical and physical properties of the thin film at the liquid-air interface are of more significance than the bulk liquid and bulk gas properties. Any factor that alters the average overall mass transfer coefficient of the surface impoundment will alter the VOC emission rate from that source. Wind has a major effect because the liquid phase resistance decreases in proportion to the square of the wind velocity. High winds therefore cause low resistance to mass transfer in the liquid phase with resulting high emissions. High winds also cause an increase in wave activity that approximates the activity of an aerator. The emission rate is also sensitive to any factor that increases the

mixing of the bulk liquid; e.g., the residence time of liquid in the surface impoundment and the velocity of any influent streams.

The VOC emission rate from quiescent liquid surfaces with a floating organic layer will differ from rates from liquid surfaces without such a layer. If the floating organic is a purely volatile material, then the rate will depend on the vapor pressure of the VOC and the mass transfer coefficient which in turn is dependent on the wind speed and the size of the source. If the floating organic layer is primarily a heavy oil that contains some VOCs, then the VOC emission rate will be lower than that for quiescent lagoons. The oil layer adds an additional resistance term to the overall mass transfer coefficient due to mass transfer in the oil phase.

Emissions from aerated liquid surfaces are generally much higher than emissions from non-aerated liquid surfaces. This is due to the increased surface area and the enhancement of the gas and liquid film mass transfer coefficients. The aeration air serves to strip out VOCs from the liquid.

### **5.2.2 Model Selection**

As previously mentioned, the models in this section were adapted from the Superfund Exposure Assessment Manual<sup>1</sup> was compiled. SEAMs presents a version of the Mackay and Leinonen model<sup>2</sup> for estimating VOC emissions from lagoons, as simplified by Farino et al.<sup>3</sup>. These models are not applicable to aerated lagoons. For such cases, use the bioremediation model present in Section 4.4 or use EPA's model for aerated surface impoundments<sup>4</sup>.

### **5.2.3 Emission Model Equation**

A simplified emission rate from a hazardous waste lagoon is:

$$ER = K C SA 0.01 \quad (\text{Eq. 5-7})$$

where: ER = emission rate [g/sec];  
K = overall mass transfer coefficient [cm/sec];  
C = compound i's liquid-phase concentration [mg/L];  
SA = surface area of lagoon [m<sup>2</sup>]; and  
0.01 = conversion factor [g/mg \* l/cm<sup>3</sup> \* cm<sup>2</sup>/m<sup>2</sup>].

The overall mass transfer coefficient of Equation 5-7 may be calculated as follows:

$$\frac{1}{K} = \frac{1}{k_L} + \frac{R T}{(H k_G)} \quad (\text{Eq. 5-8})$$

where:  $k_L$  = liquid phase mass transfer coefficient of compound i (cm/sec);  
R = ideal gas constant, equal to  $8.2 \times 10^5$  (atm-m<sup>3</sup>/mol-°K);  
T = absolute temperature (°K);  
H = Henry's Law constant of compound i (atm-m<sup>3</sup>/mol); and  
 $k_G$  = gas phase mass transfer coefficient of compound i (cm/sec).

In many cases, the gas-phase mass transfer coefficient is much larger than the liquid-phase mass transfer coefficient and can be ignored; (i.e.,  $\frac{1}{K} = \frac{1}{k_L}$ ). Default values for K are given in Section 5.2.6.

For liquid-phase mass transfer coefficients, Equations 5-9 or 5-10 may be used. The liquid-phase mass transfer coefficient can be estimated as follows:

$$k_L = \left( \frac{32}{MW} \right)^{\frac{1}{2}} \left( \frac{T}{298} \right) (k_{L,O_2}) \quad (\text{Eq. 5-9})$$

where: 32 = molecular weight of O<sub>2</sub> (g/mol);  
MW = molecular weight of compound i (g/mol); and  
 $k_{L,O_2}$  = liquid-phase mass transfer coefficient of O<sub>2</sub> (cm/sec).

At windspeeds below 3.25 m/sec (about 7 mph), the liquid-phase mass transfer coefficient can be estimated as follows:



$$k_L = 2.78 \times 10^4 [D_w / 8.5 \times 10^6]^{0.667} \quad (\text{Eq. 5-10})$$

where:  $D_w$  = diffusivity in water of compound i [ $\text{cm}^2/\text{sec}$ ]; and  
 $8.5 \times 10^6$  = empirical factor [ $\text{cm}^2/\text{sec}$ ].

The gas-phase mass transfer coefficient is typically described as:

$$k_G = (0.482)(U^{0.78})(Sc_G^{-0.67})(d_e^{-0.11}) \quad (\text{Eq. 5-11})$$

where: 0.482 = empirical constant [ $\text{cm/sec (m/sec)}^{-0.78} (\text{m})^{0.11}$ ];  
 $U$  = windspeed [ $\text{m/sec}$ ];  
 $Sc_G$  = gas side Schmidt number [unitless]; and  
 $d_e$  = effective diameter of surface impoundment [m].

The Schmidt number can be calculated as follows:

$$Sc_G = \frac{\mu_G}{\rho_G D_a} \quad (\text{Eq. 5-12})$$

where:  $\mu_G$  = viscosity of air [ $\text{g/cm-sec}$ ];  
 $\rho_G$  = density of air [ $\text{g/cm}^3$ ]; and  
 $D_a$  = diffusivity in air of compound i [ $\text{cm}^2/\text{sec}$ ].

The effective diameter of the lagoon can be calculated as follows:

$$d_e = [1.27 SA]^{0.5} \quad (\text{Eq. 5-13})$$

The gas-phase mass transfer coefficient of a compound can also be estimated using the following simplified procedure:

$$k_G = \left( \frac{18}{MW} \right)^{0.335} \left( \frac{T}{298} \right)^{1.005} (k_{G,H_2O}) \quad (\text{Eq. 5-14})$$

where: 18 = molecular weight of water [ $\text{g/mol}$ ];  
 $MW$  = molecular weight of compound i [ $\text{g/mol}$ ]; and  
 $k_{G,H_2O}$  = gas-phase mass transfer coefficient of water vapor [ $\text{cm/sec}$ ].

**Table 3-5.**

**Default Values for Thermal Incinerators**

Parameter	Symbol	Units	Default Value	Expected Range	Reference
Total feed rate of waste into unit	$F_T$	kg/hr	5,900 (soils) <sup>f</sup>	900-24,000 (soils)	8
			1,800 (liquids/sludges) <sup>f</sup>	90-13,600 (liquids/sludges)	8
Destruction and removal efficiency	DRE	%	99.99 (VOCs, organics) 99.9999 (dioxins, furans, and PCBs)	Not known	

**Table 3-6.**

**Example Scenarios for Thermal Incinerators<sup>a</sup>**

Parameter	Units	System		
		Small	Medium	Large
Feed rate (soils)	kg/hr	900-1,800	3,600-8,200	9,100-24,000
Feed rate (liquids/sludges)	kg/hr	90-550	430-3,200	900-13,600
Mass of soil to be treated	kg	$<4.5 \times 10^6$	$4.5 \times 10^6$ - $2.7 \times 10^7$	$>1.8 \times 10^7$
Gas Volume <sup>b</sup>	m <sup>3</sup> /min	50-150	150-280	280-710
	cfm	1,800-5,000	5,000-10,000	10,000-25,000
Stack Height	m	6	8	20
Stack Diameter	m	0.3	0.5	1
Exit Gas Velocity	m/sec	7	10	20
Exit Gas Temperature <sup>c</sup>	°C	70	70	70

<sup>a</sup>Assumes a rotary kiln incineration system.

<sup>b</sup>Gas volume assumes dry standard conditions at 7% O<sub>2</sub>.

<sup>c</sup>Assumes a quench and wet scrubbing system at adiabatic saturation for the stack gas.

SOURCE: Reference 8

The underlying principle behind Equation 3-5 is that the minimum DRE standard will be met. Although it is possible that the DRE might be surpassed, this will only cause the model to err on the conservative side. The required DRE may not be met during process-upset conditions and when the waste feed composition differs significantly from the waste used in any trial burns used to develop the standard operating conditions.

### 3.3.8 Example Calculations

Consider the following remediation scenario. The soil in a hypothetical site has been tested, and it contains:

PCBs	2%
1,2,4-Trichlorobenzene	2800 ppb

The contractor will use a rotary kiln incinerator with a feed rate of 6000 kg/hr. The device burns propane, which is assumed to not contribute measurably to the emissions of any of the above compounds. The exit gas flow rate is not known.

First, find the mass flow rate of contaminants into the incinerator from Equation 3-6 (note that 2% = 20,000 ppm, and that 2800 ppb = 2.8 ppm):

$$F_{\text{PCB}} = 10^6 \times 6000 \times 20,000 = 120 \text{ kg/hr};$$

$$F_{\text{TCB}} = 10^6 \times 6000 \times 2.8 = 0.017 \text{ kg/hr}.$$

Next calculate the organic emissions using Equation 3-5 and a DRE for PCBs of 99.9999%, and a DRE for TCB of 99.99%.

$$ER_{\text{PCB}} = 0.278 \times 120 \times (1 - 99.9999/100) = 3.3 \times 10^5 \text{ g/s; and}$$

$$ER_{\text{TCB}} = 0.278 \times 0.017 \times (1 - 99.99/100) = 4.7 \times 10^7 \text{ g/s}.$$

The emission rate should be compared to the total mass of the contaminant of interest to ensure that the estimated emissions over some time period do not exceed the total mass that is present. The total mass can be calculated as follows:

$$M = C * SA * l * 1.0 \quad (\text{Eq. 5-15})$$

where:      M      =      total mass of contaminant [g];  
                  l      =      depth of lagoon [m]; and  
                  1.0      =      conversion factor [g \* L / mg \* m<sup>3</sup>]

#### 5.2.4 Minimum Requirements for Field Data

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of air emissions. The minimum field data required to estimate emissions from lagoons are: are:

- Surface area of emitting area;
- Specific contaminants present in the lagoon; and
- Average contaminant concentration in the lagoon.

#### 5.2.5 Sources of Input Data

The only site specific data required to estimate emissions of VOCs from a lagoon are the concentration of the contaminants of interest in the lagoon, the surface area of the lagoon, and the wind speed (at a height of 10m). The remaining variables are generally available in Appendix A to this report. Additional information is given in References 4 through 7 on how to calculate mass transfer rates and estimate input parameters.

#### 5.2.6 Default Values for Input Variables

Table 5-2 contains default values needed for estimating VOC emissions from lagoons. Data for the viscosity and density of air at temperatures other than 25° C can be found in Reference 6; estimation methods can be found in Reference 5. Table 5-3 contains default values for the overall mass transfer coefficient.

**Table 5-2.**  
**Default Values for Estimating VOC Emissions From Lagoons**

Parameter	Symbol	Units	Default Value	Expected Range	Reference
Surface Area	SA	m <sup>2</sup>	4,050 (1 acre)	4050 - 20,200	Author's estimate
Temperature	T	°K	298	278-328	Author's estimate
Henry's Law Constant	H	atm-m <sup>3</sup> /mol	See Appendix A	--	--
Liquid-phase mass transfer coefficient of oxygen	k <sub>L,O2</sub>	cm/sec	0.002	5x10 <sup>-4</sup> -0.02	Author's estimate
Diffusivity in water	D <sub>w</sub>	cm <sup>2</sup> /sec	See Appendix A	--	--
Wind speed	U	m/sec	2.0	0-4.47	Author's estimate
Viscosity of air	μ <sub>g</sub>	g/cm-sec	1.81 x 10 <sup>-4</sup>	0.0170-0.0185	4, 6
Density of air	ρ <sub>G</sub>	g/cm <sup>3</sup>	1.21 x 10 <sup>-3</sup>	1.1034-1.2928	4, 6
Diffusivity in air	D <sub>a</sub>	cm <sup>2</sup> /sec	See Appendix A	--	--
Molecular weight	MW	g/mol	See Appendix A	--	--
Gas-phase mass transfer coefficient of water vapor	k <sub>G,H2O</sub>	cm/sec	0.83	0.0047 - 1.4	8

**Table 5-3.**  
**Default Values for Overall Mass Transfer Coefficient**

Parameter	Symbol	Units	Default Value	Reference
Overall mass transfer coefficient (by process type)	K	cm/sec	4.2 x 10 <sup>-4</sup> (quiescent surface)	4
			0.077 (turbulent surface, mechanically altered)	4
			0.34 (turbulent surface, diffused aeration)	4
Overall mass transfer coefficient* (by compound)	K	cm/sec	1.9 x 10 <sup>-3</sup> (MW = 32)	Author's estimate
			1.3 x 10 <sup>-3</sup> (MW = 64)	Author's estimate
			9.5 x 10 <sup>-4</sup> (MW = 128)	Author's estimate
			6.8 x 10 <sup>-4</sup> (MW = 256)	Author's estimate

\*Assuming H = 1 x 10<sup>3</sup>

For purposes of dispersion modeling, the default one-acre lagoon or surface impoundment from Table 5-2 can be assumed to have dimensions of 64m by 64m and a release height of 1m. As always, site-specific values should be used if available.

### **5.2.7 Model Assumptions/Sensitivity Analysis**

The emission rate of Equation 5-7 assumes a low-solubility contaminant at steady-state conditions. The liquid-phase concentration of the contaminant is assumed to be uniform throughout the lagoon, the air/water interface is assumed to be stagnant, and the air-phase concentration of the contaminant is assumed to be negligible. If the last assumption is invalid, then the original equations of Mackay and Lienonen<sup>2</sup> should be used.

It is not recommended that temperatures other than 298 °K (25° C) be used in equations 5-8 and 5-9, unless the Henry's Law constants and mass transfer coefficients are also adjusted for temperature.

### **5.2.8 Example Calculations**

A 2 acre body of water is contaminated with 3 ppm methylene chloride (dichloromethane).

To find the emission rate from Equation 5-7, the concentration will have to be expressed in units of mg/L. For dilute solutions, 1 ppm = 1 mg/L. The above concentration is thus 3 mg/L. Also, the area must be converted to m<sup>2</sup> using 1 acre = 4,046 m<sup>2</sup>, so 2 acres equals about 8,100 m<sup>2</sup>.

The overall mass transfer coefficient must be calculated using Equation 5-8. The Henry's Law constant from Appendix A is 0.00319 atm-m<sup>3</sup>/mol. The liquid-phase and gas-phase mass transfer coefficients are found using Equations 5-10 and 5-11, respectively. Default values of windspeed, viscosity of air, and density of air are

assumed. Additional inputs needed for these equations are obtained from the appendices:

$$D_w = 1.17 \times 10^5 \text{ cm}^2/\text{sec};$$

$$D_a = 0.117 \text{ cm}^2/\text{sec};$$

The Schmidt number and effective diameter of the lagoon are thus:

$$Sc_G = \frac{(1.81 \times 10^{-4})}{(1.21 \times 10^{-3})(0.117)} = 1.28$$

$$d_e = [1.27 \cdot 8,100]^{0.5} = 101 \text{ m}$$

Using these inputs, the mass transfer coefficients are:

$$k_L = (2.78 \times 10^4)(1.17 \times 10^5 / 8.5 \times 10^6)^{0.667} = 3.44 \times 10^4 \text{ cm/sec}; \text{ and}$$

$$k_G = (0.482)(2^{0.78})(1.28^{0.667})(101^{0.11}) = 0.423 \text{ cm/sec}.$$

As expected, the liquid-phase mass transfer coefficient is the rate limiting step in the overall mass transfer process. The overall mass transfer coefficient, and thus emission rate, can now be found:

$$\frac{1}{K} = \frac{1}{3.44 \times 10^{-4}} + \frac{(8.2 \times 10^{-5} \times 298)}{(0.00319)(0.423)} = 2920$$

$$\text{or } K = \frac{1}{2920} = 3.4 \times 10^{-4} \text{ cm/sec}$$

$$ER = \left( \frac{1}{2920} \right) (3)(8,100)(0.01) = 0.083 \text{ g/sec}$$

This is the estimated initial emission rate. The rate will decrease over time.

## 5.2.9 References

1. U.S. EPA. Superfund Exposure Assessment Manual (SEAMs). EPA/540/1-88/001. April 1988.
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## 5.3 SPILLS, LEAKS, AND OPEN WASTE PITS

### 5.3.1 Description of Emission Process

The emission processes from contaminated surface soils are intermediate in nature between the applicable processes for landfills and for lagoons. Surface contamination due to spills, leaks, or landtreatment results in areas of pooled waste both on and below the soil surface. The pooled waste quickly evaporates or percolates down



through the soil. The majority of the contamination becomes adsorbed onto the surface of soil particles. The emission rate is usually assumed to be controlled by the diffusion rate in the air pore space when the waste loading and soil particles are both small. In this case, the emission rate is controlled in the same manner as for covered landfills and the same considerations apply. If, however, the surface soils are tilled or otherwise disturbed, large increases in emissions will occur. This is a result of the contaminants being redistributed so that the depleted near-surface soil layer receives additional waste material. Soil disturbances also expose moist subsurface layers which leads to loss of moisture over time with a resulting increase in the air-filled porosity of the soil.

### 5.3.2 Model Selection

The Superfund Exposure Assessment Manual<sup>1</sup> uses a simplified version of the Thibodeaux and Hwang model<sup>8</sup> for estimating VOC emissions from spills, leaks, and open (uncovered) waste pits. In this model, the emission rate is controlled by the rate of diffusion through the soil. The contaminant concentration in the soil is assumed to remain constant and the contaminant release occurs by the loss of successive unimolecular layers of contaminant from the surface of the wet, or contaminated, zone. Over time, this process is assumed to result in a dry zone on increasing depth at the soil surface and a wet zone of decreasing depth below the dry zone.

### 5.3.3 Emission Model Equation

A "fresh" spill is a site with saturated surface soil. The emission rate is given by:

$$ER = k_G C_v SA 10^4 \quad (\text{Eq. 5-16})$$

where:

ER	=	emission rate of contaminant i (g/sec);
$k_G$	=	gas phase mass transfer coefficient of i (cm/s);
$C_v$	=	vapor concentration of compound i in soil pore spaces (g/cm <sup>3</sup> );
SA	=	contaminated surface area (m <sup>2</sup> ); and
$10^4$	=	conversion factor (cm <sup>2</sup> /m <sup>2</sup> ).

The emissions model for "old" spills is the same used for uncovered landfills and open waste pits:

$$ER = \frac{2 D C_1 SA 10^4}{l_d + \left[ \frac{2 D C_1 t}{C_s} + l_d^2 \right]^{\frac{1}{2}}} \quad (\text{Eq. 5-17})$$

where:

ER	=	average emission rate of compound i over time [g/sec];
D	=	phase transfer coefficient [cm <sup>2</sup> /sec];
C <sub>1</sub>	=	liquid-phase concentration of i in soil [g/cm <sup>3</sup> ];
C <sub>s</sub>	=	bulk contaminant concentration of i soil [g/cm <sup>3</sup> ];
SA	=	contaminated surface area [m <sup>2</sup> ];
10 <sup>4</sup>	=	conversion factor [cm <sup>2</sup> /m <sup>2</sup> ];
l <sub>d</sub>	=	depth of dry zone at sampling time [cm]; and
t	=	time since sampling occurred [sec].

If the contaminant has been entirely absorbed into the soil surface, soil phase mass transfer resistance is expected to be important and Equation 5-17 should be used. Note that the emission rate at the time of sampling (t = 0) is given by a simpler equation:

$$ER = \frac{D C_1 SA 10^4}{l_d} \quad (\text{Eq. 5-18})$$

An expression for the phase transfer coefficient, D, of Equation 5-17 is:

$$D = \frac{D_a E_a^{\frac{4}{3}} H}{R T} \quad (\text{Eq. 5-19})$$

where:

D <sub>a</sub>	=	diffusion coefficient of compound i in air [cm <sup>2</sup> /sec];
E <sub>a</sub>	=	total soil porosity [unitless];
H	=	Henry's Law constant of compound i [atm-m <sup>3</sup> /mol];
R	=	ideal gas constant, equal to 8.2x10 <sup>5</sup> [atm-m <sup>3</sup> /mol-°K]; and
T	=	absolute temperature [°K].

The time required from the last measurement until this point is t<sub>d</sub>, and may be calculated from:

$$(\text{Eq. 5-20})$$

$$t_d = \frac{(l_T^2 - l_d^2)}{2D} \cdot \left( \frac{C_s}{C_1} \right)$$

where:  $t_d$  = time between measurement and total volatilization [sec];  
 $l_T^2$  = depth from soil surface to bottom of contaminated region [cm].

#### 5.3.4 Minimum Requirements for Field Data

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of air emissions. The minimum field data required to estimate emissions from spill or leak sites are:

- Surface area;
- Specific contaminants present in the soil; and
- Average contaminant concentration in the soil.

#### 5.3.5 Sources of Input Data

Uncovered landfills, spills, and open waste pits as modeled in Equations 5-16 and 5-17 require some inputs previously described in Sections 5.1 and 5.2. Procedures for determining the gas-phase mass-transfer coefficient were given in Equations 5-11 and 5-14 of Section 5.2.3. The vapor concentration can be measured in the field or assumed to be equal to the saturated vapor concentration as shown in Equation 5-2 of Section 5.1.3. An equation for calculating the air-filled porosity of soil was given as Equation 5-4 in Section 5.1.3.

#### 5.3.6 Default Values for Input Variables

Default values for equations 5-16 and 5-17 are given in Table 5-4. Contaminant concentrations, depths, and areas of contamination all spill sites will vary greatly from site to site, and default values are not appropriate.

Table 5-4.  
Default Values for Estimating VOC Emissions from Spill Sites

Parameter	Symbol	Units	Default Value	Expected Range	Reference
Vapor concentration in soil pore spaces	$C_v$	g/cm <sup>3</sup>	$C_g \cdot 10^{-12}$ (see Appendix A)	—	—
Bulk density of soil	$\beta$	g/cm <sup>3</sup>	1.5	1.0 - 2.0	3
Diffusivity in air	$D_a$	cm <sup>2</sup> /sec	(see Appendix A)	—	—
Air-filled porosity of soil	$E_a$	Unitless	0.55 dry, uncompacted soil;	—	3
			0.35 wet or compacted soil;	—	3
			0.05 sludge	—	*
Henry's Law Constant	$H$	atm-m <sup>3</sup> /mol	(see Appendix A)	—	—
Temperature	$T$	°K	298	278 - 328	*
Gas-phase Mass Transfer Coefficient	$k_G$	cm/sec	0.15	0.0062-0.52	4

\*Author's estimate

For purposes of dispersion modeling, the emission source should be assumed to be a square with a release height of 1m.

### 5.3.7 Model Assumptions/Sensitivity Analysis

Equation 5-16, the "fresh" spill model, is only valid for short term emission rates. The assumption that the contaminant concentration remains constant until all of it has volatilized, results in an overprediction of the emission rate since an exponential decay in emission rate will more likely occur. The  $C_v$  term in Equation 5-16 assumes a single component spill (i.e., mole fraction equals one).

It is not recommended that temperatures other than the default temperature be used unless the Henry's Law constant and other variables that are temperature dependent are also adjusted.

### 5.3.8 Example Calculations

A site has just been contaminated with a spill of hexane and phenol. An area of approximately 1/4 acre (1,000 m<sup>2</sup>) is saturated with the two contaminants. No other information is available. The emissions can be calculated using Equation 5-16. From Table 5-3, a default value for  $k_G$  is 0.15 cm/sec and a default value for  $C_v$  is  $C_g \times 10^{12}$ . From Appendix A, the saturated vapor concentration ( $C_g$ ) for hexane is 6.96x10<sup>8</sup> ug/m<sup>3</sup> and it is 1.72x10<sup>5</sup> ug/m<sup>3</sup> for phenol. Inserting these various values into Equation 5-16 yields:

$$\begin{aligned} ER_{\text{Hexane}} &= (0.15)(6.96 \times 10^8)(10^{12})(1000)(10^4) = 1000 \text{ g/sec} \\ ER_{\text{Phenol}} &= (0.15)(1.72 \times 10^5)(10^{12})(1000)(10^4) = 0.26 \text{ g/sec} \end{aligned}$$

After six months, the spill has spread and is now found to cover an area of 1/2 acre (2,000 m<sup>2</sup>). It no longer fits the criteria of a "fresh" spill-- the liquid is not standing on the surface of the soil, and no longer saturates it. Preliminary sampling indicates a concentration of 67 µg/g phenol and 333 µg/g hexane underneath an average "dry zone"

that is 10 cm deep. Assuming a bulk density of 1.5 g/cm<sup>3</sup>, the contaminant concentrations can be converted to units of g/cm<sup>3</sup> as previously shown in Equation 4-5:

$$\begin{aligned} 67 \mu\text{g/g} * 1.5 * 10^6 &= 1.00 \times 10^4 \text{ g/cm}^3 \\ 333 \mu\text{g/g} * 1.5 * 10^6 &= 5.00 \times 10^4 \text{ g/cm}^3 \end{aligned}$$

This is assumed to equal the liquid phase concentration in the soil. The phase transfer coefficient is calculated using values of diffusivity in air and Henry's Law constant from Appendix A along with the default temperature (298° K) and the air-filled porosity.

Inserting these values into Equation 5-19 yields:

$$\begin{aligned} D(\text{phenol}) &= (0.0820)(0.55^{4/3})(4.54 \times 10^{-7}) / (8.2 \times 10^{-5})(298) = 6.87 \times 10^{-7} \\ D(\text{Hexane}) &= (0.2000)(0.55^{4/3})(0.200) / (8.2 \times 10^{-5})(298) = 0.738 \end{aligned}$$

To find the emission rate at the time the soil samples were collected, use Equation 5-18:

$$\begin{aligned} \text{ER}(\text{phenol}) &= 6.87 \times 10^{-7} * 1.00 \times 10^4 * 2000 * 10^4 / 10 = 1.4 \times 10^4 \text{ g/sec.} \\ \text{ER}(\text{hexane}) &= 0.738 * 5.00 \times 10^4 * 2000 * 10^4 / 10 = 740 \text{ g/sec.} \end{aligned}$$

### 5.3.9 References

1. U.S. EPA. Superfund Exposure Assessment Manual (SEAMs). EPA/540/1-88/001. April 1988.
2. Thibodeaux, L.J. and Hwang, S.T. Landfarming of Petroleum Waste-- Modeling the Air Emission Problem. Environ. Progress Vol. 1(1). 1982.
3. Schultz, H.L., et al. Superfund Exposure Assessment Manual. EPA/540/1-88/001. April 1988.
4. Eklund, B.M., S. Smith, and A. Hendler. Estimation of Air Impacts for the Excavation of Contaminated Soil. EPA-450/1-92-004. March 1992.

## **SECTION 6**

### **PARTICULATE MATTER, METAL, ACID GAS, AND PRIORITY POLLUTANT EMISSIONS FROM POINT SOURCES**

Simple air emission estimation procedures are presented in this section for two point sources of particulate matter (PM) and metal emissions, namely: thermal destruction units (incinerators) and thermal desorption units. The same format is followed for each source. A brief description of the emission process is given, followed by a discussion of available air emission models. The model selected for inclusion in this manual is then presented along with sources of input data and default values for each of the input variables of the selected model. The model assumptions are then briefly discussed. Finally, an example calculation is shown and references are listed.

#### **6.1 THERMAL DESTRUCTION**

##### **6.1.1 Description of Emission Process**

Thermal destruction, also known as thermal treatment, high-temperature thermal treatment, thermal oxidation, or incineration, is a very commonly used remediation at Superfund sites. Its primary advantage is that it destroys toxic organic compounds. However, a disadvantage is the generation of acid gases from halogenated organic compounds and the creation of toxic products of incomplete combustion (PIC) such as dioxins. Further, toxic metals in the waste are not controlled by incineration, so some emissions will occur.

Several types of incinerators are now in use at Superfund sites, but rotary kiln designs are the most common. The emission estimation methods presented in this section are valid for any design, but default values given are valid only for rotary-kiln incinerators. The procedures provide estimates of uncontrolled emissions. In actual practice, however, control devices for particulate matter, etc. are always used. The procedures for estimating uncontrolled emissions given in this section may be useful for estimating the required removal efficiency of a proposed control device or for estimating the size and cost of a

control device capable of achieving a given removal efficiency. Information on the effectiveness of various control devices is available<sup>1,2,3,4</sup>. The primary inorganic contaminants emitted from these types of incinerators are discussed below.

#### Particulate Matter

The waste feed, auxiliary fuel, and combustion air can all serve as sources for particulate matter emissions from an incineration system. Particle emissions may result from inorganic salts and metals that either pass through the system as solids or vaporize in the combustion chamber and recondense as solid particles in the stack gas. High molecular weight hydrocarbons may also contribute to particulate matter emissions if oxidation is not complete. Particulate matter (PM) emissions are sensitive to operating conditions, and are affected by waste composition, feed rate, PM size distribution within the waste, and incinerator design. A conservative estimate of PM emissions may be reached by assuming the maximum allowable under RCRA regulations, which is 0.08 grains/dscf (0.18 g per dry standard m<sup>3</sup>) corrected to 7% oxygen in the stack gas.

#### Metals

Toxic metals may be present within the waste feed or the soils themselves. The 10 metals identified by the US EPA<sup>5</sup> as hazardous to humans or the environment are: antimony, arsenic, barium, beryllium, cadmium, hexavalent chromium, lead, mercury, silver, and thallium. Four (arsenic, beryllium, cadmium, hexavalent chromium) are known or suspected carcinogens. The Clean Air Act Amendments address emissions of four additional metals: cobalt, manganese, nickel, and selenium.

The emission rate of a metal is affected by the partitioning of the metal within the combustion chamber. Metals in the waste feed will either remain in the solids and be discharged in the bottom ash, or they will be vaporized and carried out by combustion gases. Conservative estimates of metals partitioning in incinerators have been developed by the EPA, based on actual testing.



### Acid Gases

Halogens or sulfur in the waste stream (whether elemental or in compound form) will result in the production of acid gases during incineration. The acid gases of primary interest are hydrogen chloride (HCl), hydrogen fluoride (HF), hydrogen bromide (HBr), and sulfur dioxide (SO<sub>2</sub>). The content of halogens and sulfur in the waste and the fuel feed determine the uncontrolled emission levels of their respective acid gases. The concentrations of these elements range widely for different waste types; consequently, the resulting levels of acid gas emissions will also show wide variability. Emissions of free chlorine (Cl<sub>2</sub>) from incinerators may also be possible if there is insufficient hydrogen available to react with all of the chlorine present in the off gases.

### Other Pollutants

Achieving high levels of destruction of organic wastes is directly related to combustion chamber temperature: the higher the temperature, the greater the destruction and removal efficiency for organic compounds. Unfortunately, the fixation of nitrogen and oxygen to form oxides of nitrogen (NO<sub>x</sub>) also increases with combustion temperature. NO<sub>x</sub> emissions caused by this mechanism are referred to as thermal NO<sub>x</sub>. Additional NO<sub>x</sub> emissions, called fuel NO<sub>x</sub>, will be formed if there are bound nitrogen atoms in the waste (e.g., amine compounds). The rate of NO<sub>x</sub> formation will depend on fuel the firing rate, the amount excess oxygen, combustion temperature, and other operational controls.

Carbon monoxide (CO) monitoring of stack gases is a regulatory requirement for incinerators under RCRA. If the required DREs for organic compounds are met, CO emissions will generally be low (<100 ppmv) due to the high operating temperatures and the excess oxygen maintained in the process.

#### **6.1.2 Model Selection**

No applicable detailed models for estimating non-VOC emissions from incinerators had been identified in the preparation of this report. Eklund et al.<sup>3</sup> have developed simple mass-balance equations to estimate incinerator PM emissions. In another EPA study, IT

modified these equations slightly<sup>4</sup>, and this latter reference contains the model used here. Both documents summarize typical operating conditions, feed rates, etc., and also address metal and other inorganic emissions.

### 6.1.3 Emission Model Equation

The models presented below for PM, metals, acid gases, and priority pollutants are all for uncontrolled emission rates.

Equation 6-1 is a simple mass-balance formula which gives a conservative estimate of PM emissions from an incinerator based on the assumption that the emissions will be the maximum allowable under RCRA regulations:

$$ER = 0.18 Q \quad (\text{Eq. 6-1})$$

where:

ER	=	emission rate of particulate matter [g/sec];
0.18	=	maximum allowable PM emissions in stack [g/dscm]; and
Q	=	exit gas flow rate [dry standard m <sup>3</sup> /sec].

Equation 6-2 provides an emission rate estimate for metals:

$$ER = 0.278 F_m \left( \frac{PF}{100} \right) \quad (\text{Eq. 6-2})$$

where:

ER	=	emission rate of metal [g/sec];
0.278	=	conversion factor [g/sec / Kg/hr];
F <sub>m</sub>	=	feed rate of metal [kg/hr]; and
PF	=	partitioning factor of metal [%].

To calculate emission rates of acid gases, a conservative assumption may be made: if all of the acid-forming element in the halogenated compounds reacts with hydrogen present in the combustion chamber, the stoichiometric ratio will predict the amount of acid gas produced. Thus:

$$ER = 0.278 F_a r \quad (\text{Eq. 6-3})$$

where: ER = emission rate of acid gas i [g/sec];  
0.278 = conversion factor [g/sec / kg/hr];  
F<sub>a</sub> = feed rate of halogen or sulfur [kg/hr]; and  
r = stoichiometric ratio of acid-gas-to-element [unitless].

Stoichiometric ratios of acid-gas-to-element for several common elements are given in Section 6.1.5. The stoichiometric ratio for sulfur dioxide to sulfur is also included; the partitioning of sulfur to sulfuric acid and sulfur dioxide is not known, so it is assumed that all sulfur is converted to SO<sub>2</sub>, and no H<sub>2</sub>SO<sub>4</sub> is formed and no sulfur leaves in the bottom ash.

The feed rates of elements in the waste stream may be calculated from Equations 6-4 and 6-5 if the total feed rate and concentration of compounds containing acid-forming elements is known. An analogous equation can be used for estimating the feed rate of metal species.

$$F_a = F_T C_a 10^{-6} \quad (\text{Eq. 6-4})$$

where: F<sub>T</sub> = total feed rate [kg/hr];  
C<sub>a</sub> = concentration of acid in feed rate [μg/g]; and  
10<sup>-6</sup> = conversion factor [g/μg].

The total feed rate will depend on whether the waste being treated is a solid or liquid. If sulfur is present in the auxiliary fuel, the feed rate of sulfur from the fuel must be added to the feed rate of sulfur from the waste to obtain the total feed rate of sulfur.

$$C_a = \sum_{i=1}^n \left\{ C_i \left( \frac{MW_A}{MW_i} \right) \right\} \quad (\text{Eq. 6-5})$$

where: C<sub>a</sub> = concentration of acid-forming element in the waste [μg/g];  
C<sub>i</sub> = concentration of compound i containing above element [μg/g];  
MW<sub>a</sub> = molecular weight of acid-forming element [g/mol]; and  
MW<sub>i</sub> = molecular weight of compound i containing above element [g/mol].

If an ultimate analysis of the waste has been performed, the concentration of each element will be known and the use of Equation 6-5 will not be necessary.

#### **6.1.4 Minimum Requirements for Field Data**

The minimum field data required to estimate emissions from thermal treatment systems are:

- Specific contaminants present in the soil or waste to be treated;
- Average contaminant concentration in the soil or waste; and
- Maximum contaminant concentration in the soil or waste.

#### **6.1.5 Sources of Input Data**

The preferred source of input data for Equation 6-1 through 6-4 is field measurements for the thermal destruction system of interest. At the very least, field data should be obtained regarding the specific contaminants present in the material to be treated and their average and maximum concentration. Values for the flow rate of material to the incinerator and the efficiency of any control devices may be obtained from design specification documents and blueprints or from field measurements. Once the incineration unit is in operation, stack sampling of emissions from the system can be performed to confirm the emission estimates.

#### **6.1.6 Default Values for Input Variables**

Table 6-1 gives default values to be used in the emission estimation equations for a typical rotary-kiln incinerator. Table 6-2 lists some conservative estimates of metals partitioning in incinerators for several metals. Table 6-3 presents information regarding stack parameters for a relatively small incinerator to assist in the prediction of downwind ambient air concentrations using an EPA-approved air dispersion model.

**Table 6-1.**  
**Default Values for Estimating Emissions from Incinerators**

Parameter	Symbol	Units	Default Value	Expected Range
Exit gas flow rate	Q	ds <sup>3</sup> /sec	4.8 <sup>b</sup>	0.83 - 11.8
Total feed rate	F <sub>T</sub>	kg/hr	5,000 solids <sup>a</sup> 1,500 liquids <sup>a</sup>	900-24,000 solids 90-13,600 liquids/sludges
Stoichiometric ratio	r	unitless	1.013 HBr/Br	--
			1.028 HCl/Cl	--
			1.053 HF/F	--
			1.998 SO <sub>2</sub> /S	--

<sup>a</sup>Assumes 15,000,000 Btu/hr capacity.

<sup>b</sup>Equals 50,000 ACFM at 2,200° F

SOURCE: Reference 4

**Table 6-2.**  
**Default Values for Estimating Metal Partitioning**

Parameter	Symbol	Units	Default Value	Comments
Metal Partitioning	PF	%	100 (liquids)	Beryllium Chromium Antimony Arsenic Barium Cadmium Lead Mercury Silver Thallium
			5 (solids)	
			100 (solids)	

SOURCE: Reference 4

**Table 6-3.**  
**Stack Parameters for Rotary Kiln Incinerators**

Parameter	Range	Default Value
Physical stack height	6 - 20 m	8 m
Stack diameter	0.3 - 1.0 m	0.5 m
Exit velocity	1400 - 4000 ft/min	2000 ft/min
	7 - 20 m/s	10 m/s
Exit temperature <sup>a</sup>	150° - 180° F	160° F
	338° - 355° K	344° K

<sup>a</sup>Assumes a quench and wet scrubbing system at adiabatic saturation of the stack gas. Assumes an exit gas rate of 3700 dscf/min or 1.7 ds<sup>3</sup>/sec).

SOURCE: Reference 4

### 6.1.7 Model Assumptions/Sensitivity Analysis

The emission estimation equation assumes the waste material is fed into the process unit at a constant rate and that the material is uniformly contaminated. The former assumption is reasonable, but the waste material will certainly have a degree of variability in the contaminants present and their concentrations.

The model's assumption of partitioning constants for metals is also conservative. For an added level of conservativeness, all chromium in the exit gas can be assumed to be in the hexavalent state.

For PM emissions, the assumption that the minimum regulated standard will met, but not exceeded, is obviously a conservative assumption.

### 6.1.8 Example Calculations

A site is to be remediated using incineration to destroy organic compounds that are present in soil. An ultimate analysis of the soil shows it to contain: 1.0% S, 0.5% Cl, 0.15% Ba, and 0.08% Pb. The contractor will use a rotary kiln incinerator with a feed rate of 1000 kg/hr. The device burns propane, which is assumed to not contribute measurably to the emissions of any of the above inorganic compounds. The exit gas flow rate is not known.

For PM emissions, Equation 6-2 requires an exit gas flow rate. Since this is not known, the default value will be used but it will be adjusted for the known feed rate. Since in Table 6-1 a feed rate of 5,000 kg/hr yields a flow rate of 4.8 m<sup>3</sup>/sec, this incinerator will have an exit gas rate of:

$$(1,000/5,000) \times 4.8 = 0.96 \text{ dsm}^3/\text{sec}$$

The PM emissions are then:

$$\text{ER} = 0.18 \times 0.96 = 0.17 \text{ g/sec.}$$

The metals emission rates are found in a similar manner. The feed rate of the metals are found by multiplying the total feed rate by the percentage of metal in the waste:

$$F_{Ba} = 1000 \times 0.15/100 = 1.5 \text{ kg/hr; and}$$
$$F_{Pb} = 1000 \times 0.08/100 = 0.8 \text{ kg/hr.}$$

The partitioning factor for both metals is 100%. The emission rates are then:

$$E_{Ba} = 0.278 \times 1.5 \times 100/100 = 0.42 \text{ g/sec; and}$$
$$E_{Pb} = 0.278 \times 0.8 \times 100/100 = 0.22 \text{ g/sec.}$$

The feed rates of Cl and S are:

$$F_{Cl} = 1000 \times 0.5/100 = 5.0 \text{ kg/hr; and}$$
$$F_S = 1000 \times 1.0/100 = 10 \text{ kg/hr.}$$

Their stoichiometric ratios, from Table 6-1, are 1.028 for HCl and 1.998 for SO<sub>2</sub>:

$$E_{HCl} = 0.278 \times 5.0 \times 1.028 = 1.4 \text{ g/sec; and}$$
$$E_{SO_2} = 0.278 \times 10 \times 1.998 = 5.5 \text{ g/sec.}$$

#### 6.1.9 References

1. Eklund, et al. Control of Air Toxics at Superfund Sites. Report to EPA's Center for Environmental Research Information. June 1992.
2. Eklund, et al. Air Emissions From the Treatment of Soils Contaminated With Petroleum Fuels and Other Substances. EPA-600/R-92-124. July 1992.
3. U.S. EPA. Air/Superfund National Technical Guidance Study Series, Volume III: Estimation of Air Emissions from Cleanup Activities at Superfund Sites. Report No. EPA-450/1-89-003. NTIS PB89 180061/AS. January 1989.
4. IT Corp. Screening Procedures For Estimating the Air Impacts of Incineration at Superfund Sites. EPA Contract No. 68-02-4466, WA 91-77. September 1991.
5. U.S. EPA. Technical Background Document: Control of Metals and HCl Emissions from Hazardous Waste Incinerators. August 1989.

## **6.2 THERMAL DESORPTION**

Little information about emissions of non-organic compounds from thermal desorption units is available. Therefore, it is recommended that the procedures for incineration be used with slightly different default values in some cases.

### **6.2.1 Description of Emission Process**

Thermal desorption is distinguished from thermal incineration chiefly by the operating conditions of the equipment. The operating temperatures are much lower, so the fraction of metals that partition to the vapor phase is lower. Given the lower temperatures, the formation of NO<sub>x</sub> should be less of a concern. Also, the volume of exit gas may be somewhat smaller, and if so, there will be less particulate matter carry over.

### **6.2.2 Model Selection**

No applicable detailed models for estimating non-VOC emissions from thermal desorption units had been identified in the preparation of this report. Eklund et al.<sup>1</sup> have developed simple mass-balance equations to estimate incinerator PM, metal, and inorganic gas emissions. In another EPA study, IT modified these equations slightly<sup>2</sup>, and this latter contains the model used here. Although written for incinerators, these mass balance equations are general in nature, and are applicable to desorption as to incineration.

### **6.2.3 Default Values for Input Variables**

Table 6-4 contains feed rates and other default parameters applicable to thermal desorption units<sup>3</sup>. The feed rate and exit gas values are based on a single system; the use of process-specific data is strongly recommended. For all other parameters, the default values given in Section 6.1.6 for incinerators should be used.



**Table 6-4.**

**Default Values for Estimating Emissions from Thermal Desorption Units**

Parameter <sup>a</sup>	Symbol	Units	Default Value	Expected Range	Reference
Total feed rate	F <sub>T</sub>	kg/hr	27,200	2,700 - 90,800	2
Exit gas flow rate	Q	ds <sup>3</sup> /sec	8.8	1.8 - 16.2	3
PM Loading in Stack Emissions	--	g/dscm	0.46 <sup>b</sup>	--	3
		g/dscm	0.08 <sup>c</sup>	0.01 - 0.17	3
Metal partitioning	PF	%	100 - Mercury 20 - Lead 10 - Beryllium 10 - Chromium 10 - Copper 10 - Iron 10 - Zinc	--	4

<sup>a</sup>Use default values given in Section 6.1.6 for incinerators for all other parameters.

<sup>b</sup>Asphalt plant

<sup>c</sup>Rotary dryer

SOURCE: Reference 3

#### 6.2.4 References

1. U.S. EPA. Air/Superfund National Technical Guidance Study Series, Volume III: Estimation of Air Emissions from Cleanup Activities at Superfund Sites. Report No. EPA-450/1-89-003. NTIS PB89 180061/AS. January 1989.
2. IT Corp. Screening Procedures For Estimating the Air Impacts of Incineration at Superfund Sites. EPA Contract No. 68-02-4466, WA 91-77. September 1991.
3. Eklund, et al. Air Emissions From the Treatment of Soils Contaminated With Petroleum Fuels and Other Substances. EPA-600/R-92-124. July 1992.
4. de Percin, P. (EPA). Personal communication from Paul de Percin to Bart Eklund of Radian Corporation. August 1992.

## **SECTION 7**

### **PARTICULATE MATTER AND METAL EMISSIONS FROM AREA SOURCES**

Simple air emission estimation procedures are presented in this section for area sources of particulate matter (PM) and metals, including: materials handling and other area sources such as solidification/stabilization (S/S), storage piles, and dry surface impoundments. The same format is followed for each source. A brief description of the emission process is given, followed by a discussion of available air emission models. The model selected for inclusion in this manual is then presented along with sources of input data and default values for each of the input variables of the selected model. The model assumptions are then briefly discussed. Finally, an example calculation is shown and references are listed.

#### **7.1 MATERIALS HANDLING**

Emission estimation procedures are given below for transfer operations, waste mixing, grading, and traffic on paved and unpaved roads.

##### **7.1.1 Description of Emission Process**

Materials handling is a very common source of particulate matter emissions at Superfund sites; excavation of soils, soil transport, dumping and formation of soil storage piles, and grading are all routinely performed. The PM emissions arising from these operations should be evaluated, whether the material is contaminated or not since PM emissions (less than 10 microns in diameter) are a criteria pollutant.

##### **7.1.2 Model Selection**

Few emissions models for PM from materials handling exist which meet the criteria of this manual. Compilations<sup>1,2,3</sup> of such models produced by the EPA have themselves been produced by Cowherd et al.<sup>4</sup>. This latter document contains a comprehensive collection of

empirically based screening models and was used as the principal source of all models in this section as well as Section 7.2.

### 7.1.3 Emission Model Equation

The emissions of PM from all transfer operations - adding to or removing from piles, conveyor belts, truck dumping - are expressed in Equation 7-1:

$$E = \frac{k (0.0016)(M) \left( \frac{U}{2.2} \right)^{1.3}}{\left( \frac{X_{H_2O}}{2} \right)^{1.4}} \quad (\text{Eq. 7-1})$$

where:

E	=	emissions [g];
k	=	particle size multiplier [unitless];
0.0016	=	empirical constant [g/Kg]; and
M	=	mass of waste handled [Kg];
U	=	mean wind speed [m/sec];
2.2	=	empirical constant [m/sec]; and
X <sub>H<sub>2</sub>O</sub>	=	percent moisture content [%].

Reference 1 provides a more detailed equation for this same activity that takes into account the drop height, the silt content of the material, and the capacity of the dump bucket. The particle size multiplier, k, for several sizes of particles are:

size	multiplier
< 50 um	1.0
< 30 um	0.74
< 15 um	0.48
< 10 um	0.35
< 5 um	0.20
< 2.5 um	0.11

For emissions from the erosion of intermittently active piles, use erosion equation 7-9 from Section 7.2 for each period between activity; use the above equation during the activity itself.

For emissions during materials handling involving mixing and tilling (waste incorporation and cultivation), a simple model is:

$$E = k (0.00538) SA 10^{-4} (s)^{0.6} \quad (\text{Eq. 7-2})$$

where: E = emissions [g];  
k = particle size multiplier (0.21 for PM<sub>10</sub>) [unitless];  
0.00538 = empirical constant [g/hectare];  
10<sup>-4</sup> = conversion factor [hectare/m<sup>2</sup>];  
SA = area treated [m<sup>2</sup>]; and  
s = percent silt content [%].

If wastes or soil are being graded by a bulldozer or any other tractor with a blade, then the following equation should be used to predict the PM<sub>10</sub> (particulate matter of less than 10 microns) emissions:

$$ER = \frac{0.094 s^{1.5}}{X_{H_2O}^{1.4}} \quad (\text{Eq. 7-3})$$

where: ER = PM<sub>10</sub> emission rate [g/sec];  
0.094 = empirical constant [g/sec];  
s = percent silt content [%]; and  
X<sub>H<sub>2</sub>O</sub> = percent moisture content [%].

The emission rate of traffic on paved roads in grams per vehicle kilometers traveled (VKT) is given by Equation 7-4.

$$EF = 220 \left( \frac{sL}{12} \right)^{0.3} \quad (\text{Eq. 7-4})$$

where: EF = PM<sub>10</sub> emission factor [g/VKT];  
220 = empirical constant [g/VKT];  
sL = silt surface loading [g/m<sup>2</sup>];  
12 = empirical constant [g/m<sup>2</sup>]; and  
0.3 = empirical constant [unitless].

For unpaved roads, the emission model is given by Equation 7-5:

$$EF = 610 \left( \frac{s}{12} \right) \left( \frac{S}{48} \right) \left( \frac{W}{2.7} \right)^{0.7} \left( \frac{w}{4} \right)^{0.5} \frac{(365 - p)}{365} \quad (\text{Eq. 7-5})$$

where:

EF	=	emission factor [g/VKT];
610	=	empirical constant [g/VKT];
s	=	percent silt content of road surface [%];
12	=	empirical constant [unitless];
S	=	mean vehicle speed [km/hr];
48	=	empirical constant [km/hr];
W	=	mean vehicle weight [Mg];
2.7	=	empirical constant [Mg];
w	=	mean number of wheels per vehicle [unitless];
4	=	empirical constant [unitless];
365	=	no. of days per year [days]; and
p	=	number of days with < 0.01 inches precipitation [days].

The emission factors can be converted into a total mass emitted if multiplied by the number of vehicle kilometers traveled.

If the dust is contaminated, the PM emission rates of Equations 7-1 through 7-3 may be translated to emission rates of the contaminant as follows:

$$EF_i = X_i EF \quad (\text{Eq. 7-6})$$

where:

EF <sub>i</sub>	=	emission factor of contaminant i [g/VKT]; and
X <sub>i</sub>	=	fraction of contaminant i in particulate matter [unitless].

In general, the dust and silt at a site will contain a higher fraction of the metal species than the bulk soil at the site; i.e. the particulate matter is enriched with the metals. Therefore, x<sub>i</sub> is equal to:

$$x_i = C Z 10^{-6} \quad (\text{Eq. 7-7})$$

where:

C	=	concentration of metal in the bulk soil [μg/g];
Z	=	enrichment factor [unitless]; and
10 <sup>-6</sup>	=	conversion factor [g/μg].

#### **7.1.4 Minimum Requirements for Field Data**

Site-specific field data must be collected (e.g., during the RI/FS) to provide the input data necessary to generate reasonably accurate estimates of particulate matter emissions. The minimum field data required to estimate emissions for the various sources covered in this section are:

- Transfer operations: percent moisture content of the material;
- Mixing and tilling: area treated and silt content of soil;
- Grading: percent moisture content and silt content of material;
- Traffic on paved roads: silt surface loading;
- Traffic on unpaved roads: silt content of road surface; and
- Metal emissions for any operation: average concentration of metal in bulk soil.

#### **7.1.5 Sources of Input Data**

Aerodynamic particle size multipliers for Equation 7-1 are provided in Section 7.1.3. In general, meteorological data will be available from an on-site monitoring station. If not, meteorological data may be obtained from a local airport or government monitoring station. Soil data is available from the state agricultural service or the federal Soil Conservation Service.

#### **7.1.6 Default Values for Input Variables**

Default values for equation input parameters are provided in Table 7-1. Some input variables, such as mass of material handled and surface area graded, are extremely site- and operation-specific, so no default values for these variables are given. Table 7-2 contains default values for metal enrichment of soils for use in Equation 7-7. Figure 7-1 shows a geographic map of areas of the U.S. and the average number of days with >0.01 inch of precipitation annually.

Table 7-1.

## Default Values for Estimating Emissions from Materials Handling

Parameter	Symbol	Units	Default Value	Expected Range	Reference
Mean wind speed	U	m/sec	4.4	0 - 4.47	*
Moisture content	X <sub>H2O</sub>	%	10	--	*
Silt content	s	%	8 (<75 $\mu$ m)	2 - 20	4
Silt surface loading	sL	g/m <sup>2</sup>	5	0.3 - 30	4
Mean vehicle speed	S	km/hr	20	8 - 45	4
Mean vehicle weight	W	Mg	3 (plant vehicle)	2 - 9	4
			20 (Commercial haulers)	9 - 45	4
			30 (plant haul trucks)	20 - 50	4
Mean # of wheels	w	unitless	10	4 - 18	4

\* = Author's estimate.

Table 7-2.

## Metal Concentration and Enrichment Data (Z)

	Median Enrichment Ratios (Z)
Arsenic (As)	1.28
Barium (Ba)	1.85
Cadmium (Cd)	1.31
Chromium (Cr)	4.72
Lead (Pb)	7.34
Mercury (Hg)	3.00
Selenium (Se)	2.00
Silver (Ag)	1.00

Source: Reference 6



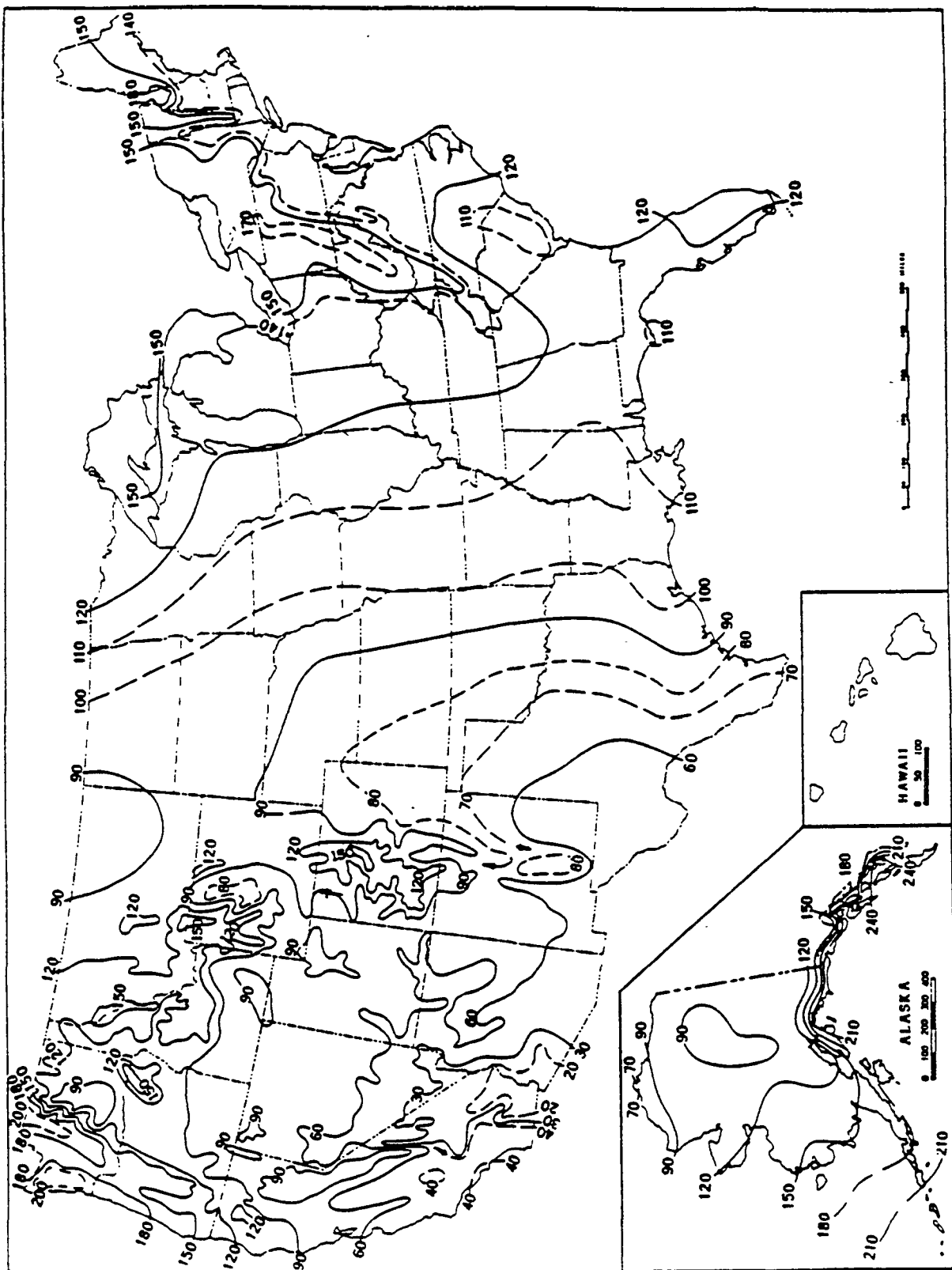


Figure 7-1. Mean Annual Number of Days With At Least 0.01 inches of Precipitation.

### 7.1.7 Model Assumptions/Sensitivity Analysis

These models are equally applicable to a wide variety of materials handling activities. They are based on the premise that a certain percentage of a soil's surface area has a high "erosion potential", and that the rest of the surface will not be emitted. The equations presented in this section are all empirically based and drawn from measurements at actual sites; they are meant to predict the behavior of average sites. If a particular site has unusual meteorological conditions, rubble, debris, or high silt content of soil, etc., these model accuracy may be affected. It is prudent to always monitor actual field emissions, at least from some test location, to verify the model predictions.

### 7.1.8 Example Calculations

Assume that a Superfund site exists in Durham, NC and soil is excavated from a pit and transported to a storage pile 500 m away. The backhoe moves 4 m<sup>3</sup> of soil at a time, and 10 truckloads a day are moved with each truck containing 20 m<sup>3</sup> of soil. In addition, a bulldozer works over the storage pile for an hour each day. The soil moisture content is 10% and the average wind speed at the site is 2 m/sec. The lead content of the soil is 100 µg/g.

To find the total PM<sub>10</sub> emissions from this site, first convert the 20 m<sup>3</sup> of soil for ten trucks to a mass, using the default soil density of 1.5 g/cm<sup>3</sup>:

$$20 \text{ m}^3 \times 1.5 \text{ g/cm}^3 \times 10^6 \text{ cm}^3/\text{m}^3 \times 10 \text{ trucks} = 300,000 \text{ kg/soil.}$$

The particle size multiplier for <10 µm is 0.20. Use Equation 7-1 for the backhoe emissions:

$$ER = 0.20 * (0.0016) * 300,000 * (2/2.2)^{1.3} / (10/2)^{1.4} = 8.9 \text{ g.}$$

This number should be multiplied by 2, because the soil will be dumped once into the trucks and dumped a second time onto the storage pile. Thus the total emissions from dumping are 18 g and the average emission rate is 18 g/day.

To find the lead emissions from the backhoe operations, first calculate the fraction of lead in the windblown dust using Equation 7-7 with the lead content of the soil (100 ug/g) and the enrichment factor for lead from Table 7-2 (7.34):

$$X_i = (100)(7.34)(10^{-6}) = 7.34 \times 10^{-4} \text{ (g lead/g windblown dust)}$$

This value is then used with the average emission rate calculated above (18 g/day) and Equation 7-6:

$$EF_{\text{lead}} = (7.34 \times 10^{-4})(18) = 0.013 \text{ g/day.}$$

To find the  $PM_{10}$  emissions from transport, the silt content of the unpaved surface is needed, as well as the number of wheels/truck. Assume that both equal the default values from Table 7-1. The number of days with precipitation > 1" for North Carolina is found from Figure 7-1. From Equation 7-5, the transport emissions are:

$$EF = 610 (8/12) (20/48) (25/2.7)^{0.7} (10/4)^{0.5} (365 - 120)/365 = 850 \text{ g/km.}$$

A total of 10 truckloads are driven over a 1 km roundtrip, so the total emissions (ignoring the weight difference between the empty and full truck) are 11,000 g or 11 kg. The average emission rate is 11 kg/day.

Finally, to find the emission rate due to the bulldozing, use Equation 7-3:

$$ER = \frac{0.094 (8)^{1.5}}{(10)^{1.4}} = 0.085 \text{ g/sec}$$

Since the activity is underway for one hour, the total emissions are about 300 g.

### **7.1.9 References**

1. U.S. EPA. AP-42: Compilation of Air Pollutant Emission Factors, Fourth Edition. U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC. September 1985.
2. Cowherd, C., G. Muleski, P. Englehart, and D. Gillette. Rapi Assessment of Exposure to Particulate Emissions from Surface Contamination Sites. EPA/600-8-85/002. February 1985.
3. Englehart, P. and D. Wallace. Assessment of Hazardous Waste TSDF Particulate Emissions. EPA Contract No. 68-02-3891. October 1986.
4. Cowherd, C., P. Englehart, G. Muleski, and J. Kinsey. Hazardous Waste TSDF Fugitive Particulate Matter Air Emissions Guidance Document. EPA 450/3-89-019. May 1989.
5. Cowherd, C., et al. Development of Emission Factors for Fugitive Dust Sources. EPA/450/3-74/037. 1974.
6. Eklund, B., et al. Air/Superfund National Technical Guidance Study Series. Volume III. Estimation of Air Emissions from Cleanup Activities at Superfund Sites. EPA-450/1-89-003. NTIS PB89. 1800 GI/AS. January 1989.

## **7.2 OTHER AREA SOURCES OF PM and METAL EMISSIONS**

### **7.2.1 Description of Emission Process**

Fugitive dust may be released from a variety of origins other than materials handling. A remediation activity that may be a significant area sources of fugitive dust is solidification/stabilization. Non-remediation sources include storage piles and dry impoundments.

### **7.2.2 Model Selection**

Equations based on fundamental physical laws have been reported for windblown dust<sup>1,2</sup>, but the most widely accepted equations are those empirically derived by Cowherd, et al.<sup>3,4,5</sup>, which are still in current use by the Superfund program<sup>6</sup>. The most suitable equations

for inclusion in this manual are those given by Cowherd, et al.<sup>7</sup> for open waste piles and staging areas, dry surface impoundments, and waste stabilization. These are incorporated in the manual along with the metal enrichment factors for dust presented in Volume III of the National Technical Guidance Series (NTGS) documents<sup>8</sup>.

### 7.2.3 Emission Model Equation

A simple model of erosion from level areas such as dry surface impoundments during a time period  $t$  between disturbances is given by:

$$ER = \frac{k \ SA \ p_t}{t \ 86,400} \quad (\text{Eq. 7-8})$$

where:

ER	=	emission rate from surface material during period $t$ [g/sec];
k	=	particle size multiplier [unitless];
SA	=	area of contamination [m <sup>2</sup> ];
$p_t$	=	erosion potential corresponding to fastest mile of wind during period $t$ [g/m <sup>2</sup> ];
$t$	=	no. of days between disturbances [day]; and
86,400	=	conversion factor [sec/day].

Particle size multipliers for Equation 7-8 are:

Size	Multiplier
< 30 um	1.0
< 15 um	0.6
< 10 um	0.5
< 2.5 um	0.2

Total suspended particulates (TSP) from wind erosion of continuously active piles can be estimated as:

$$EF = 1.9 \left( \frac{s}{15} \right) \frac{(365 - p)}{235} \left( \frac{f}{15} \right) \quad (\text{Eq. 7-9})$$

where: EF = emission factor (g/m<sup>2</sup>-day);  
0.19 = empirical constant (g/m<sup>2</sup>-day);  
s = percentage silt of aggregate (%);  
1500 = empirical constant (unitless);  
365 = no. of days/year (days);  
p = number of days of precipitation > 0.01 inch per year (days);  
235 = empirical constant (days);  
f = fraction of time wind > 5.4 m/sec at mean pile height (unitless); and  
15 = empirical constant (unitless).

The fraction of TSP that is PM<sub>10</sub> can be assumed to be 50%. Equation 7-9 is valid for piles that are active at least once per day.

The emissions of PM from stabilization and solidification have been found to be over 1 kg/hr for full-scale operations. No equations, however, are available for estimating PM emissions from the actual mixing process. An emission factor has been published that can be converted into an emission estimation equation:<sup>8</sup>

$$ER = (0.05)(Q)(2.78 \times 10^{-4}) \quad (\text{Eq. 7-10})$$

where: ER = emissions (g/sec);  
0.05 = emission factor (g/kg);  
Q = treatment rate (kg/hr); and  
2.78x10<sup>-4</sup> = conversion factor (hr/sec).

PM emissions from the transfer of the stabilized waste can be estimated as:

$$E = \frac{0.00056 \left( \frac{U}{2.2} \right)^{1.3} (M)}{\left( \frac{X_{H_2O}}{2} \right)^{1.4}} \quad (\text{Eq. 7-11})$$

where: E = emissions [g];  
0.00056 = empirical factor [g/kg];  
U = wind speed [m/sec];  
2.2 = empirical factor [m/sec];  
M = mass of material handled [kg];  
X<sub>H<sub>2</sub>O</sub> = moisture fraction [%]; and  
2 = empirical factor [%].

#### **7.2.4 Minimum Requirements for Field Data**

The minimum field data required to estimate emissions for the various sources covered in this section are:

- Dry surface impoundments: surface area of contamination and the number of days between disturbances;
- Continuously active piles: percentage silt of aggregate and the fraction of time with high winds; and
- Stabilization and solidification: percent moisture content and mass of material handled.

#### **7.2.5 Sources of Input Data**

Procedures for calculating the erosion potential are given in Appendix B. For other variables, see the discussion in Section 7.1.5.

#### **7.2.6 Default Values for Input Variables**

Table 7-3 provides default values for the input parameters needed for Equations 7-8 and 7-9. For Equation 7-11, the fraction of TSP made up of  $PM_{10}$  is estimated to be 0.5.

#### **7.2.7 Model Assumptions/Sensitivity Analysis**

These emission models assume that after a disturbance, only a certain fraction of the soil's surface will erode, regardless of the time exposed. That is why Equation 7-8 does not depend on time, except for the length of the period between disturbances. Equation 7-9 is for continuously active disturbances, and so it assumes that at any point in time, a disturbance has just occurred, and the same fraction is able to erode.

For in-place contaminated soil, over-prediction of the emissions is possible as a soil crust tends to form, reducing the erosibility of the pile or field.

Table 7-3.

## Default Values for Estimating PM Emissions from Other Area Sources

Parameter	Symbol	Units	Default Value	Expected Range	Reference
Surface area	SA	m <sup>2</sup>	2000	Site specific	—
Erosion potential	P <sub>i</sub>	g/m <sup>2</sup>	33	0 - 525 (see Appendix B)	7
Percentage of silt	s	%	2.2	0.44 - 19	7
Fraction of time with high winds	f	unitless	20	Site specific	—
Wind speed	U	m/sec	4.4	0.6 - 6.7	7
Moisture fraction	X <sub>H<sub>2</sub>O</sub>	%	2	0.25 - 4.8	7
Treatment Rate	Q	kg/hr	45,000	4,500 - 120,000	—



### 7.2.8 Example Calculations

A site in Raleigh, NC contains a one acre dry surface impoundment. The soil has a silt content of 8%. The soil is excavated every other day, placed in an (active) storage pile, and then fed into a stabilization process. The storage pile has a surface area of 2000 m<sup>2</sup>. One thousand kilograms per day of the stabilized material is placed in a lined portion of the dry surface impoundment.

The particulate matter emissions from the excavation and transfer (dumping) operations can be calculated using procedures previously described. Example calculations for particulate matter emissions of less than 10 microns from the other sources are given below.

Emissions from the surface impoundment are estimated using Equation 7-8. The surface area of the impoundment is one acre or 4050 m<sup>2</sup>. The particle size multiplier for < 10 μm is 0.5, the time between disturbances is two days, and the default erosion potential is 33 g/m<sup>2</sup>. The emission rate from the surface impoundment is:

$$ER = \frac{(0.5)(4050)(33)}{(2)(86,400)} = 0.39\text{g/sec}$$

Particulate matter from wind erosion of continuously active piles can be estimated using Equation 7-9. The number of rainy days from Figure 7-1 is 55:

$$EF_{TSP} = \frac{1.9 \left( \frac{8}{15} \right) (365 - 55)}{235 \left( \frac{20}{15} \right)} = 1.78 \text{ g/m}^2\text{-day}$$

Assuming 50% of the TSP is PM<sub>10</sub>, the emissions of PM<sub>10</sub> from the storage pile are:

$$ER = (1.78)(50/100)(2000) = 1800 \text{ g/day.}$$

The emissions of PM emissions from the transfer of the stabilized waste can be estimated using Equation 7-11:

$$E = \frac{0.00056 \left( \frac{4.4}{2.2} \right)^{1.3} (1,000)}{\left( \frac{2}{2} \right)^{1.4}} = 1.4 \text{ g (per day)}$$

The total daily emissions from transfer are thus:

$$ER = \frac{(2.29 \cdot 10^{-7} \text{ g/kg})(1000 \text{ kg})}{1 \text{ day}} = 2.3 \cdot 10^{-4} \text{ g/day}$$

## 7.2.9 References

1. Momeni, M.H., Y. Yuan, and A.J. Zielen. The Uranium Dispersion and Dosimetry (UDAD) Code. U.S. NRC. NTIS NUREG/CR-0553. May 1979
2. RTI. A Method for Estimating Fugitive Particulate Emissions from Hazardous Waste Sites. EPA/600/2-87/066. NTIS PB87-232203. August 1987.
3. U.S. EPA. User's Guide - Emission Control Technologies and Emission Factors for Unpaved Road Fugitive Emissions. EPA/625/5-87/022. September 1987.
4. U.S. EPA. AP-42: Compilation of Air Pollutant Emission Factors, Fourth Edition. U.S. EPA, Office of Air Quality Planning and Standards, Research Triangle Park, NC. September 1985.
5. Cowherd, C., G. Muleski, P. Englehart, and D. Gillette. Rapi Assessment of Exposure to Particulate Emissions from Surface Contamination Sites. EPA/600-8-85/002. February 1985.
6. U.S. EPA. Guideline for Predictive Baseline Emissions Estimation Procedures for Superfund Sites, Interim Final. Environmental Quality Management, Inc. January 1992.
7. Cowherd, C., P. Englehart, G. Muleski, and J. Kinsey. Hazardous Waste TSD Fugitive Particulate Matter Air Emissions Guidance Document. EPA 450/3-89-019. May 1989.
8. Eklund, B., et al. Air/Superfund National Technical Guidance Study Series, Volume III: Estimation of Air Emissions from Cleanup Activities at Superfund Sites. Report No. EPA-450/1-89-003. NTIS PB89 180061/AS. January 1989.

## APPENDIX A

# APPENDIX A - PHYSICAL PROPERTY DATA

No.	Organic Compound	CAS NO.	Formula	Molecular Weight (g/g-mol)	Vapor Pressure (mm Hg)*	Diffusivity in Air (cm <sup>2</sup> /sec)	Saturated Vapor Conc. (µg/m <sup>3</sup> )*	Henry's Law Constant		Maximum Water Solubility (mg/L)	Diffusivity in Water (cm <sup>2</sup> /sec)	Log Kow
								H*	Log H			
1	Acetaldehyde	75-07-0	C <sub>2</sub> H <sub>4</sub> O	44.00	760	0.1240	1.80E+09	9.50e-05	-4.02	inf	1.41e-05	--
2	Acetic acid	64-19-7	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	60.06	15.41	0.1300	4.97E+07	6.27e-02	-1.20	inf	1.20e-05	--
3	Acetic anhydride	108-24-7	C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>	102.09	5.266	0.2350	2.89E+07	5.91e-06	-5.23	--	9.33e-06	--
4	Acetone	67-64-1	C <sub>3</sub> H <sub>6</sub> O	58.08	266	0.1240	8.30E+08	2.50e-05	-4.60	inf	1.14e-5	-0.24
5	Acetonitrile	75-05-8	C <sub>2</sub> H <sub>3</sub> N	41.06	90	0.1280	1.99E+08	5.80e-06	-5.24	inf	1.66e-5	-0.34
6	Acrolein	107-02-8	C <sub>3</sub> H <sub>4</sub> O	56.1	244.2	0.1050	7.36E+08	5.66e-05	-4.25	208,000	1.22e-5	--
7	Acrylic acid	79-10-7	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	72.1	5.2	0.0908	2.02E+07	1.00e-07	-7.00	inf	1.08e-5	0.13
8	Acrylonitrile	107-13-1	C <sub>3</sub> H <sub>3</sub> N	53.06	114	0.1220	3.25E+08	8.80e-05	-4.06	73,500	1.34e-5	-0.92
9	Allyl alcohol	107-18-6	C <sub>3</sub> H <sub>6</sub> O	58.08	23.3	0.1140	7.27E+07	1.80e-05	-4.74	inf	1.14e-5	-0.22
10	Allyl chloride	107-05-1	C <sub>3</sub> H <sub>5</sub> Cl	76.53	368	0.0	1.51E+09	3.71e-01	-0.43	3,600	0.0	--
11	Aniline	62-53-3	C <sub>6</sub> H <sub>7</sub> N	93.13	1	0.0700	5.01E+06	2.60e-06	-5.59	35,000	8.3e-6	--
12	Anthracene	120-12-7	C <sub>14</sub> H <sub>10</sub>	178.23	1.3E-06	0.0	1.25E+01	6.75e-02	-1.17	1.3	0.0	4.45
13	Benzaldehyde	100-52-7	C <sub>7</sub> H <sub>6</sub> O	106.12	1	--	5.70E+06	4.23e-05	-4.37	3,000	--	--
14	Benzene	71-43-2	C <sub>6</sub> H <sub>6</sub>	78.12	95.2	0.0932	4.00E+08	5.50e-03	-2.26	1,780	9.8e-6	2.12
15	Benzoic acid	65-85-0	C <sub>7</sub> H <sub>6</sub> O <sub>2</sub>	122.12	0.00704	0.0	4.62E+04	1.82e-08	-7.74	2,900	7.97e-6	--
16	Benzyl alcohol	100-51-6	C <sub>7</sub> H <sub>8</sub> O	108.14	0.15	--	8.72E+05	6.10e-07	-6.21	35,000	--	--
17	Benzyl chloride	100-44-7	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	126.6	1.21	0.0750	8.23E+06	4.33e-04	-3.36	1,619	7.8e-6	2.63
18	Bromoform	75-25-2	CHBr <sub>3</sub>	252.77	5.6	0.0	7.61E+07	5.94e-04	-3.23	3,190	0.0	--
19	1,3-Butadiene	106-99-0	C <sub>4</sub> H <sub>6</sub>	54.09	2100	0.2490	6.09E+09	1.42e-01	-0.85	735	1.8e-5	1.99
20	N-Butane	106-97-8	C <sub>4</sub> H <sub>10</sub>	58.12	1820	0.2490	5.69E+09	2.91e-01	-0.54	61	--	--
21	2-Butanol	15892-23-6	C <sub>4</sub> H <sub>10</sub> O	74.12	10		3.98E+07	2.20e-06	-5.66	184,000	--	--
22	N-Butanol	71-36-3	C <sub>4</sub> H <sub>10</sub> O	74.12	6.5	0.0800	2.59E+07	2.20e-06	-5.66	77,000	9.3e-6	--
23	N-Butyl-Acetate	123-86-4	C <sub>8</sub> H <sub>16</sub> O <sub>2</sub>	116.16	15	0.0	9.37E+07	1.64e-04	-3.79	14,000	0.0	--
24	Tert-Butyl-Alcohol	75-65-0	C <sub>4</sub> H <sub>10</sub> O	74.12	0.17		6.77E+05	2.20e-06	-5.66	inf	--	--
25	Carbon disulfide	75-15-0	CS <sub>2</sub>	76.13	366	0.1040	1.50E+09	1.68e-02	-1.77	2,900	1.0e-5	2.00
26	Carbon tetrachloride	56-23-5	CCl <sub>4</sub>	153.82	113	0.0632	9.34E+08	3.00e-02	-1.52	800	8.8e-6	2.83
27	Carbonyl sulfide	463-58-1	COS	60.1	--		--				--	--

# Appendix A. (Continued)

No.	Organic Compound	CAS NO.	Formula	Molecular Weight (g/g-mol)	Vapor Pressure (mm Hg) <sup>a</sup>	Diffusivity in Air (cm <sup>2</sup> /sec)	Saturated Vapor Conc. (μg/m <sup>3</sup> ) <sup>a</sup>	Henry's Law Constant		Maximum Water Solubility (mg/L)	Diffusivity in Water (cm <sup>2</sup> /sec)	Log Kow
								H <sup>b</sup>	Log H			
28	Catechol	120-80-9	C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub>	110.1	--	--	--				--	--
29	Chlorine	7782-50-5	Cl <sub>2</sub>	70.9	--	--	--				--	--
30	Chlorobenzene	108-90-7	C <sub>6</sub> H <sub>5</sub> Cl	112.56	11.8	0.0730	7.14E+07	3.93e-03	-2.41	488	8.7e-6	2.84*
31	Chlorodifluoromethane	75-45-6	CHClF <sub>2</sub>	86.47	--	--	--	1.00e-01	-1.00	2	--	--
32	Chloroform	67-66-3	CHCl <sub>3</sub>	119.38	208	0.0888	1.33E+09	3.39e-03	-2.47	9,300	1.0e-5	1.97*
33	Chloromethyl methyl ether	107-30-2	C <sub>2</sub> H <sub>5</sub> Cl <sub>0</sub>	80.51	--	--	--	9.12x10 <sup>-6</sup>	-5.04	2.5x10 <sup>6</sup>	--	0.0
34	Chloropentafluoroethane	76-15-3	C <sub>2</sub> ClF <sub>5</sub>	154.47	--	--	--	2.45e-01	-0.61	--	--	--
35	Chloroprene	126-99-8	C <sub>4</sub> H <sub>5</sub> Cl	88.5	273	0.1040	1.12E+09	3.35e-01	-0.475	--	1.0e-5	--
36	M-Cresol	108-39-4	C <sub>7</sub> H <sub>8</sub> O	108.14	0.08	0.0740	4.65E+05	4.43e-07	-6.35	25,000	1.0e-5	1.97
37	O-Cresol	95-48-7	C <sub>7</sub> H <sub>8</sub> O	108.14	0.24	0.0740	1.40E+06	2.60e-06	-5.59	31,000	8.3e-6	--
38	P-Cresol	106-44-5	C <sub>7</sub> H <sub>8</sub> O	108.14	0.11	0.0740	6.39E+05	4.43e-07	-6.35	24,000	1.0e-5	--
39	Cyanogen	460-19-5	C <sub>2</sub> N <sub>2</sub>	52.04	3980	--	1.11E+10	4.96e-03	-2.30	9,300	--	--
40	Cyclohexane	110-82-7	C <sub>6</sub> H <sub>12</sub>	84.16	100	0.0839	4.52E+08	1.37e-02	-1.86	100	9.1e-6	3.44
41	Cyclohexanol	108-93-0	C <sub>6</sub> H <sub>12</sub> O	100.16	1.22	0.2140	6.57E+06	4.47e-06	-5.35	38,200	8.31e-6	1.23
42	Cyclohexanone	108-94-1	C <sub>6</sub> H <sub>10</sub> O	98.14	4.8	0.0784	2.53E+07	4.13e-06	-5.38	23,000	8.62e-6	--
43	Cyclohexene	110-83-8	C <sub>6</sub> H <sub>10</sub>	82.15	--	--	--	1.03e+01	1.01	213	--	2.86
44	Cyclopentane	287-92-3	C <sub>5</sub> H <sub>10</sub>	70.13	317.44	--	1.20E+09	1.00e-02	-2.00	156	--	--
45	Diazomethane	334-88-3	CH <sub>2</sub> N <sub>2</sub>	42.04	--	--	--			?	--	--
46	Dibutyl-O-Phthalate	84-74-2	C <sub>16</sub> H <sub>22</sub> O <sub>4</sub>	278.35	1.00E-05	0.0439	--	2.80e-07	-6.55	400	7.8e-6	5.60
47	O-Dichlorobenzene	95-50-1	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	147.00	1	0.0690	7.90E+06	1.94e-03	-2.71	145	7.9e-6	3.60
48	P-Dichlorobenzene	106-46-7	C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	147.00	1.2	0.0690	9.48E+06	1.60e-03	-2.80	79	7.9e-6	3.38
49	Dichloroethylether	111-44-4	C <sub>4</sub> H <sub>8</sub> Cl <sub>2</sub> O	143.02	1.4	--	1.08E+07			?	7.9e-6	3.39
50	Dichlorodifluoromethane	75-71-8	CCl <sub>2</sub> F <sub>2</sub>	120.91	4870	0.0	3.16E+10	4.01e-01	-0.40	280	0.0	2.16
51	1,1-Dichloroethane	75-34-3	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	98.96	234	0.0919	1.24E+09	1.54e-02	-1.81	5,500	9.9e-6	1.79
52	1,2-Dichloroethane	107-06-2	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	98.96	80	0.1040	4.26E+08	1.20e-03	-2.92	8,690	9.9e-6	1.48
53	1,1-Dichloroethylene	75-35-4	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	96.94	600	0.1040	3.13E+09	2.59e-02	-1.59	210	--	1.84
54	cis-1,2-Dichloroethylene	156-59-2	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	96.94	208	--	1.08E+09	4.55e-03	-2.34	800	--	0.70

# Appendix A. (Continued)

No.	Organic Compound	CAS NO.	Formula	Molecular Weight (g/g-mol)	Vapor Pressure (mm Hg)*	Diffusivity in Air (cm <sup>2</sup> /sec)	Saturated Vapor Conc. (µg/m <sup>3</sup> )*	Henry's Law Constant		Maximum Water Solubility (mg/L)	Diffusivity in Water (cm <sup>2</sup> /sec)	Log Kow
								H <sup>b</sup>	Log H			
55	trans-1,2-Dichloroethylene	156-60-5	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	96.94	324		1.69E+09	9.46e-03	-2.02	600	—	0.48
56	Dichloromethane	75-09-2	CH <sub>2</sub> Cl <sub>2</sub>	84.93	362	0.117	1.65E+09	3.19e-03	-2.50	16,700	1.17 x 10 <sup>-5</sup>	1.30
57	Dichloromonofluoromethane	75-43-4	CHCl <sub>2</sub> F	102.92	1360	0.0	7.52E+09	9.21e+02	2.96	0.2	0.0	
58	1,2-Dichloropropane	78-87-5	C <sub>3</sub> H <sub>6</sub> Cl <sub>2</sub>	112.99	42	0.0782	2.55E+08	2.30e-03	-2.64	2,700	8.73e-6	2.00
59	1,3-Dichloropropene	542-75-6	C <sub>3</sub> H <sub>4</sub> Cl <sub>2</sub>	110.98	43	0.0	2.57E+08	2.33e-06	-5.63	2,700	0.0	2.00
60	1,2-Dichloro-1,1,2,2-Tetrafluoroethane	76-14-2	C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub>	170.92	—		—	2.45e-01	-0.61	137	—	2.82
61	Diethanolamine	111-42-2	C <sub>4</sub> H <sub>11</sub> NO <sub>2</sub>	105.14	—		—			(61)?	—	—
62	Diethyl amine	109-89-7	C <sub>4</sub> H <sub>11</sub> N	73.14	350@35C	—	1.38E+09	7.31e-03	-2.14	20,000	—	—
63	Diethyl ether	602-97-6	C <sub>4</sub> H <sub>10</sub> O	74.12	440@20C	0.0782	1.75E+09	2.65e-04	-3.58	60,400	8.61e-6	—
64	Dimethylamine	124-40-3	C <sub>2</sub> H <sub>7</sub> N	45.08	563 @ 0C	—	1.36E+09	5.24e-06	-5.28	—	—	-0.38
65	N,N-Dimethylaniline	121-69-7	C <sub>9</sub> H <sub>11</sub> N	121.18	—		—			(63)?	—	—
66	Dimethyl formamide	68-12-2	C <sub>3</sub> H <sub>7</sub> NO	73.09	4.0	0.0939	1.57E+07	1.92e-05	-4.72	20,000	1.03e-5	—
67	1,1-Dimethyl hydrazine	57-14-7	C <sub>2</sub> H <sub>8</sub> N <sub>2</sub>	60.10	157	0.1060	5.07E+08	1.24e-04	-3.91	100,000	1.09e-5	-1.32
68	2,4-Dinitrophenol	51-28-5	C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>5</sub>	184.11	53.8	0.0	5.32E+08	1.53e-07	-6.82	19,500	0.0	1.50
69	1,4-Dioxane	123-91-1	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88.11	37	0.2290	1.75E+08	2.31e-05	-4.64	inf	1.02e-5	0.01
70	Diphenyl	92-52-4	C <sub>12</sub> H <sub>10</sub>	154.21	—		—	1.01e-01	-1.00	7.5	—	—
71	Epichlorohydrin	106-89-8	C <sub>3</sub> H <sub>5</sub> ClO	92.53	17	0.0860	8.45E+07	3.23e-05	-4.49		9.08e-6	0.15
72	1,2-Epoxybutane	106-88-7	C <sub>4</sub> H <sub>8</sub> O	72.0	—		—			(72)?	—	—
73	Ethanol	64-17-5	C <sub>2</sub> H <sub>6</sub> O	46.07	50	0.1230	1.24E+08	3.03e-05	-4.52	inf	1.30e-5	-0.32
74	Ethyl acetate	141-78-6	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	88.11	100	—	4.74E+08	1.28e-04	-3.89	79,000	—	—
75	Ethyl acrylate	140-88-5	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	100.12	40	0.0770	2.15E+08	3.50e-04	-3.46	—	—	—
76	Ethyl amine	75-04-7	C <sub>2</sub> H <sub>7</sub> N	45.08	1057		2.56E+09	5.24e-06	-5.28	inf	—	—
77	Ethylbenzene	100-41-4	C <sub>8</sub> H <sub>10</sub>	106.16	10	0.0750	5.71E+07	6.44e-03	-2.19	152	7.8e-6	3.15
78	Ethyl Bromide	74-96-4	C <sub>2</sub> H <sub>5</sub> Br	108.97	—		—	1.00e-02	-2.00	—	—	—
79	Ethyl carbamate	51-79-6	C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	89.09	10		4.79E+07			(79)?	—	—
80	Ethyl Chloride	75-00-3	C <sub>2</sub> H <sub>5</sub> Cl	64.51	1200	0.2710	4.16E+09	1.40e-02	-1.85	5,740	1.15e-5	—
81	Ethylenediamine	107-15-3	C <sub>2</sub> H <sub>8</sub> N <sub>2</sub>	60.10	10.7	—	3.46E+07	8.46e-06	-5.07	inf	—	—

# Appendix A. (Continued)

No.	Organic Compound	CAS NO.	Formula	Molecular Weight (g/g-mol)	Vapor Pressure (mm Hg) <sup>a</sup>	Diffusivity in Air (cm <sup>2</sup> /sec)	Saturated Vapor Conc. (µg/m <sup>3</sup> ) <sup>a</sup>	Henry's Law Constant		Maximum Water Solubility (mg/L)	Diffusivity in Water (cm <sup>2</sup> /sec)	Log Kow
								H <sup>b</sup>	Log H			
82	Ethylene dibromide	106-93-4	C <sub>2</sub> H <sub>4</sub> Br	187.88	14	0.0	1.41E+08			inf	0.0	1.76
83	Ethylene glycol	107-21-1	C <sub>2</sub> H <sub>6</sub> O <sub>2</sub>	62.07	0.13	0.1080	4.34E+05	1.03e-07	-6.99	inf	1.22e-5	--
84	Ethylene imine	151-56-4	C <sub>2</sub> H <sub>5</sub> N	43.07	--	--	--	4.54e-04	-3.34	inf	-	--
85	Ethylene oxide	75-21-8	C <sub>2</sub> H <sub>4</sub> O	44.06	1250	0.1040	2.96E+09	1.42e-04	-3.85	--	1.45e-5	-0.22
86	Formaldehyde	50-00-0	CH <sub>2</sub> O	30.03	3500	0.1780	5.65E+09	5.76e-05	-4.24	550,000	1.98e-5	0.0
87	Formic acid	64-18-6	CH <sub>2</sub> O <sub>2</sub>	46.03	42	0.0790	1.04E+08	7.00e-07	-6.15	inf	1.37e-6	0.54
88	Furan	110-00-9	C <sub>4</sub> H <sub>4</sub> O	68.08	596	0.1040	2.18E+09	5.76e-03	-2.27	10,000	1.22e-5	--
89	Glycerol	56-81-5	C <sub>3</sub> H <sub>8</sub> O <sub>3</sub>	92.09	1.60E-04	0.0	7.92E+02	1.94e-08	-7.89	10,000	0.0	--
90	N-Heptane	142-82-5	C <sub>7</sub> H <sub>16</sub>	100.2	46	0.0	2.48E+08	2.02e+00	0.31	3	0.0	--
91	N-Hexane	110-54-3	C <sub>6</sub> H <sub>14</sub>	86.18	150.3	0.2000	6.96E+08	0.122	-0.91	13	7.77e-6	--
92	Hydrazine	302-01-2	H <sub>4</sub> N <sub>2</sub>	32.05	14.4	--	2.48E+07	6.66e-07	-6.18	--	--	-3.08
93	Hydrochloric acid	7647-01-0	HCl	36.46	32,450		6.36E+10			(93)?	--	--
94	Hydrogen cyanide	74-90-8	CHN	27.03	--	--	--	4.65e-07	-6.33	inf	--	--
95	Hydrogen sulfide	7783-06-4	H <sub>2</sub> S	34.08	15,200	0.1760	2.78E+10			4,000	--	--
96	Isobutanol	78-83-1	C <sub>4</sub> H <sub>10</sub> O	74.12	10	0.0860	3.98E+07	2.20e-06	-5.66	95,000	2.20e-6	--
97	Isobutyl acetate	110-19-0	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	116.16	--	--	--	1.64e-04	-3.79	6,300	--	--
98	Isopropyl alcohol	67-63-0	C <sub>3</sub> H <sub>8</sub> O	60.1	42.8	0.0980	1.38E+08	1.50e-04	-3.82	inf	1.04e-5	-0.16/0.28
99	Isopropyl amine	75-31-0	C <sub>3</sub> H <sub>9</sub> N	59.11	460		1.46E+09	3.58e-04	-3.45	100,000	--	--
100	Isopropylbenzene	98-82-8	C <sub>9</sub> H <sub>12</sub>	120.19	10.9@40C		7.04E+07	6.59e-03	-2.18	50	--	--
101	Methanol	67-56-1	CH <sub>4</sub> O	32.04	114	0.1500	1.96E+08	2.70e-06	-5.57	inf	1.64e-5	--
102	Methyl acetate	79-20-9	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	74.08	235	0.1040	9.36E+08	1.02e-04	-3.99	194,000	1.00e-5	--
103	Methyl acrylate	96-33-3	C <sub>4</sub> H <sub>7</sub> O <sub>2</sub>	86.09	--	--	--	1.44e-07	-6.84	60,000	--	--
104	Methyl amine	74-89-5	CH <sub>3</sub> N	31.06	770@ -6C		1.29E+09	5.38e-03	-2.27	11,500	--	--
105	Methyl bromide	74-83-9	CH <sub>3</sub> Br	94.94	--	--	--	2.21e-01	-0.66	17,500	--	--
106	Methyl-tert-butyl-ether	1634-04-4	C <sub>5</sub> H <sub>12</sub> O	88.15	245	0.0806	1.16E+09	5.92e-04	-3.23	48,000	8.026e-6	0.26
107	Methyl chloride	74-87-3	CH <sub>3</sub> Cl	50.49	3830	0.1260	1.04E+10	8.14e-03	-2.09	6,360	6.5e-6	0.95
108	Methylcyclohexane	108-87-2	C <sub>7</sub> H <sub>14</sub>	98.19	43	--	2.27E+08	9.79e-01	-0.01	14	--	--

# Appendix A. (Continued)

No.	Organic Compound	CAS NO.	Formula	Molecular Weight (g/g-mol)	Vapor Pressure (mm Hg) <sup>a</sup>	Diffusivity in Air (cm <sup>2</sup> /sec)	Saturated Vapor Conc. (μg/m <sup>3</sup> ) <sup>a</sup>	Henry's Law Constant		Maximum Water Solubility (mg/L)	Diffusivity in Water (cm <sup>2</sup> /sec)	Log Kow
								H <sup>b</sup>	Log H			
109	Methyl-ethyl-ketone	78-93-3	C <sub>4</sub> H <sub>8</sub> O	72.11	100	0.0808	3.88E+08	2.16e-04	-3.67	275,000	0.98e-5	1.74±0.12
110	Methyl formate	107-31-3	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	60.05	500	—	1.61E+09	1.30e-01	-0.89	304	—	—
111	Methyl hydrazine	60-34-4	CH <sub>6</sub> N <sub>2</sub>	46.07	49.6	—	1.23E+08	3.44e-06	-5.46	inf	—	—
112	Methyl iodide	74-88-4	CH <sub>3</sub> I	141.94	91	—	—	2.53e-03	-2.60	14,000	—	—
113	Methyl-Isobutyl-Ketone	108-10-1	C <sub>6</sub> H <sub>12</sub> O	100.16	19.31	0.0750	1.04E+08	4.95e-05	-4.31	19,000	7.08e-6	—
114	Methyl isocyanate	624-83-9	C <sub>2</sub> H <sub>3</sub> NO	57.05	348	—	1.07E+09	—	—	**	—	—
115	Methyl-Isopropyl-Ketone	563-80-4	C <sub>7</sub> H <sub>14</sub> O	86.13	15.7	0.0750	7.27E+07	4.58e-04	-3.34	47,000	0.78e-05	—
116	Methyl mercaptan	74-93-1	CH <sub>4</sub> S	48.1	—	—	—	4.18e-03	-2.38	23,300	—	—
117	Methyl methacrylate	80-62-6	C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>	100.10	39	0.0770	2.10E+08	6.60e-05	-4.18	15,000	8.50e-6	0.79
118	Methyl-N-Propyl-Ketone	107-87-9	C <sub>7</sub> H <sub>14</sub> O	86.13	—	—	—	4.58e-04	-3.34	—	—	—
119	Alpha-Methyl-Styrene	98-83-9	C <sub>9</sub> H <sub>10</sub>	118.18	0.076	0.2640	4.83E+05	5.91e-03	-2.23	2	—	—
120	Monoethanolamine	141-43-5	C <sub>2</sub> H <sub>7</sub> NO	61.08	—	—	—	3.22e-07	-6.49	100,000	—	—
121	Morpholine	110-91-8	C <sub>4</sub> H <sub>9</sub> NO	87.12	10.08	0.0910	4.72E+07	5.73e-05	-4.24	inf	9.60e-6	-1.08
122	Naphthalene	91-20-3	C <sub>10</sub> H <sub>8</sub>	128.19	0.023	0.0590	1.58E+05	4.80e-04	-3.32	30	7.50e-6	3.01/3.45
123	2-Nitropropane	79-46-9	C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	89.09	12.9	—	6.18E+07	2.23e-04	-3.65	100,000	—	—
124	N-Nitrosodimethylamine	62-75-9	C <sub>2</sub> H <sub>6</sub> N <sub>2</sub> O	74.08	—	—	—	3.0x10 <sup>-8</sup>	-7.52	1.2x10 <sup>7</sup>	—	—
125	N-Nitrosomorpholine	59-89-2	C <sub>4</sub> H <sub>8</sub> N <sub>2</sub> O	116.11	—	0.0590	—	—	—	0.059	1.00e-5	—
126	N-Nonane	111-84-2	C <sub>9</sub> H <sub>20</sub>	128.26	4.28	—	2.95E+07	4.48e-01	-0.35	79	—	—
127	N-Octane	111-65-9	C <sub>8</sub> H <sub>18</sub>	114.23	17	0.0	1.04E+08	3.87e+00	0.59	20	0.0	—
128	N-Pentane	109-66-0	C <sub>5</sub> H <sub>12</sub>	72.15	513	—	1.99E+09	1.22e-01	-0.91	360	—	—
129	Phenanthrene	85-01-8	C <sub>14</sub> H <sub>10</sub>	178.23	2.00E-04	0.0	1.92E+03	6.05e-03	-2.22	0.82	0.0	4.46
130	Phenol	108-95-2	C <sub>6</sub> H <sub>6</sub> O	94.11	0.0341	0.0820	1.72E+05	4.54e-07	-6.34	80,000	9.10e-6	1.46
131	Phosgene	75-44-5	CCl <sub>2</sub> O	98.92	1,394	0.1080	7.41E+09	1.71e-01	-0.767	slightly	1.12e-6	—
132	Phosphine	7803-51-2	H <sub>3</sub> P	34.00	2,000	—	3.66E+09	—	—	6,200	—	—
133	Phthalic anhydride	85-44-9	C <sub>8</sub> H <sub>4</sub> O <sub>3</sub>	148.11	0.0015	0.0710	1.19E+04	9.00e-07	-6.05	153,000	8.60e-6	—
134	Propane	74-98-6	C <sub>3</sub> H <sub>8</sub>	44.1	7600	—	1.80E+09	2.20e-02	-1.66	2,000	—	2.36
135	1,2-Propanediol	57-55-6	C <sub>3</sub> H <sub>8</sub> O <sub>2</sub>	76.11	0.3	—	—	1.50e-06	-5.82	20,000	—	—



# Appendix A. (Continued)

No.	Organic Compound	CAS NO.	Formula	Molecular Weight (g/g-mol)	Vapor Pressure (mm Hg) <sup>a</sup>	Diffusivity in Air (cm <sup>2</sup> /sec)	Saturated Vapor Conc. (μg/m <sup>3</sup> ) <sup>a</sup>	Henry's Law Constant		Maximum Water Solubility (mg/L)	Diffusivity in Water (cm <sup>2</sup> /sec)	Log Kow
								H <sup>b</sup>	Log H			
136	1-Propanol	71-23-8	C <sub>3</sub> H <sub>8</sub> O	60.1	20.85		6.74E+07	1.50e-04	-3.82	inf	--	--
137	beta-Propiolactone	57-57-8	C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>	72.06	3.4	--	1.32E+07			350,000	--	--
138	Propionaldehyde	123-38-7	C <sub>3</sub> H <sub>6</sub> O	58.08	300	0.102	9.37E+08	1.15e-06	-5.94	200,000	1.14e-5	--
139	Propionic acid	79-09-4	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	74.08	10	--	3.98E+07	4.87e-05	-4.31	inf	--	--
140	N-Propyl-Acetate	109-60-4	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>	102.12	35	0.0	1.92E+08	2.94e-04	-3.53	20,400	0.0	--
141	Propylene oxide	75-56-9	C <sub>3</sub> H <sub>6</sub> O	58.08	524.5	0.1040	1.64E+09	1.34e-03	-2.87	30,000	1.00e-5	--
142	1,2-Propylenimine	75-55-8	C <sub>3</sub> H <sub>7</sub> N	54.1	112		3.26E+08			(142)?	--	-0.48
143	Pyridine	110-86-1	C <sub>5</sub> H <sub>5</sub> N	79.1	20	0.0910	8.50E+07	2.36e-05	-4.63	inf	8.10e-6	0.66
144	Quinone	106-51-4	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub>	108.09	--		--			(144)?	--	--
145	Styrene	100-42-5	C <sub>8</sub> H <sub>8</sub>	104.15	7.3	0.0710	4.09E+07	2.61e-03	-2.58	300	8.00e-6	2.95
146	1,1,1,2-Tetrachloro-2,2-Difluoroethane	76-11-9	C <sub>2</sub> Cl <sub>4</sub> F <sub>2</sub>	203.83	--		--	2.45e-01	-0.61	--	--	--
147	1,1,2,2,-Tetrachloroethane	79-34-5	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	167.85	6.5	0.0710	5.86E+07	2.50e-04	-3.60	2,900	7.90e-6	2.39
148	Tetrachloroethylene	127-18-4	C <sub>2</sub> Cl <sub>4</sub>	165.83	19	0.0720	1.69E+08	2.90e-02	-1.54	150	8.2e-6	2.60*
149	Tetrahydrofuran	109-99-9	C <sub>4</sub> H <sub>8</sub> O	72.11	72.1	0.0980	2.79E+08	4.90e-05	-4.31	inf	1.05e-5	--
150	Toluene	108-88-3	C <sub>7</sub> H <sub>8</sub>	92.14	30	0.0870	1.49E+08	6.68e-03	-2.18	515	8.60e-6	2.73
151	P-Toluidine	106-49-0	C <sub>7</sub> H <sub>9</sub> N	107.16	0.3	--	1.73E+06	1.91e-05	-4.72	7,400	--	--
152	1,1,1-Trichloroethane	71-55-6	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	133.41	123	0.0780	8.82E+08	1.74e-02	-1.76	4,400	8.8e-6	2.5
153	1,1,2-Trichloroethane	79-00-5	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	133.41	25	0.0792	1.79E+08	7.40e-04	-3.13	4,500	8.80e-6	2.47
154	Trichloroethylene	79-01-6	C <sub>2</sub> HCl <sub>3</sub>	131.4	75	0.0790	5.30E+08	9.10e-03	-2.04	1,100	9.10e-6	2.38
155	Trichlorofluoromethane	75-69-4	CCl <sub>3</sub> F	137.37	667	0.0870	4.92E+09	5.83e-02	-1.23	1,100	9.70e-6	2.53
156	1,2,3-Trichloropropane	96-18-4	C <sub>3</sub> H <sub>3</sub> Cl <sub>3</sub>	147.43	3.1	0.0710	2.46E+07	2.80e-02	-1.55	--	7.90e-6	--
157	1,1,2-Trichloro-1,2,2-Trifluoroethane	76-13-1	C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub>	187.38	300	0.0780	3.02E+09	2.45e-01	-0.61	170	8.20e-6	2.00
158	Triethylamine	121-44-8	C <sub>6</sub> H <sub>15</sub> N	101.19	400	--	2.18E+09	2.66e-03	-2.58	20,000	--	--
159	Trifluorobromomethane	75-63-8	CBRF <sub>3</sub>	148.91	--		--	1.00e-01	-1.00	--	--	--
160	1,2,3-Trimethylbenzene	526-73-8	C <sub>9</sub> H <sub>12</sub>	120.19	--		--	1.47e-01	-0.83	--	--	--
161	1,2,4-Trimethylbenzene	95-63-6	C <sub>9</sub> H <sub>12</sub>	120.19	--		--	1.47e-01	-0.83	57	--	--
162	1,3,5-Trimethylbenzene	108-67-8	C <sub>9</sub> H <sub>12</sub>	120.19	1.86	--	1.20E+07	1.47e-01	-0.83	20	--	--

# Appendix A. (Continued)

No.	Organic Compound	CAS NO.	Formula	Molecular Weight (g/g-mol)	Vapor Pressure (mm Hg) <sup>a</sup>	Diffusivity in Air (cm <sup>2</sup> /sec)	Saturated Vapor Conc. (μg/m <sup>3</sup> ) <sup>a</sup>	Henry's Law Constant		Maximum Water Solubility (mg/L)	Diffusivity in Water (cm <sup>2</sup> /sec)	Log Kow
								H <sup>b</sup>	Log H			
163	Vinyl Acetate	108-05-4	C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>	86.09	115	0.0850	5.32E+08	6.20e-04	-3.21	20,000	9.20e-6	--
164	Vinyl bromide	593-60-2	C <sub>2</sub> H <sub>3</sub> Br	107.0	895		5.15E+09			(164)?	--	--
165	Vinyl-Chloride	75-01-4	C <sub>2</sub> H <sub>3</sub> Cl	62.5	2660	0.0900	8.94E+09	8.60e-02	-1.07	1.1	1.04e-5	1.38
166	M-Xylene	108-38-3	C <sub>8</sub> H <sub>10</sub>	106.2	8	0.0700	4.57E+07	5.20e-03	-2.28	200	7.80e-6	3.26
167	O-Xylene	95-47-6	C <sub>8</sub> H <sub>10</sub>	106.2	7	0.0870	4.00E+07	5.27e-03	-2.28	175	1.00e-5	2.95
168	P-Xylene	106-42-3	C <sub>8</sub> H <sub>10</sub>	106.2	9.5	0.0	5.42E+07	5.27e-03	-2.28	198	0.0	3.15

<sup>a</sup> At 25°C.

<sup>b</sup>  $H \left( \frac{\text{atm} \cdot \text{m}}{\text{mol}} \right)$



**APPENDIX B**

**PROCEDURES FOR CALCULATING EROSION POTENTIAL**

**Source:** Cowherd, C., P. Englehart, G. Muleski, and J. Kinsey. Hazardous Waste TSD Fugitive Particulate Matter Air Emissions Guidance Document. EPA-450/3-89-019 (NTIS PB90-103250). May 1989.

### 3.2.2 Wind Erosion

Dust emissions may be generated by wind erosion of open waste piles and exposed areas within a disposal facility. These sources typically are characterized by nonhomogeneous surfaces impregnated with nonerodible elements (particles larger than approximately 1 cm in diameter). Field testing of coal piles and other exposed materials using a portable wind tunnel has shown that (a) threshold wind speeds exceed 5 m/s (11 mph) at 15 cm above the surface or 10 m/s (22 mph) at 7 m above the surface, and (b) particulate emission rates tend to decay rapidly (half life of a few minutes) during an erosion event. In other words, these aggregate material surfaces are characterized by finite availability of erodible material (mass/area) referred to as the erosion potential. Any natural crusting of the surface binds the erodible material, thereby reducing the erosion potential.

3.2.2.1 Emissions and Correction Parameters. If typical values for threshold wind speed at 15 cm are corrected to typical wind sensor height (7-10 m), the resulting values exceed the upper extremes of hourly mean wind speeds observed in most areas of the country. In other words, mean atmospheric wind speeds are not sufficient to sustain wind erosion from flat surfaces of the type tested. However, wind gusts may quickly deplete a substantial portion of the erosion potential. Because erosion potential has been found to increase rapidly with increasing wind speed, estimated emissions should be related to the gusts of highest magnitude.

The routinely measured meteorological variable which best reflects the magnitude of wind gusts is the fastest mile. This quantity represents the wind speed corresponding to the whole mile of wind movement which has passed by the 1-mi contact anemometer in the least amount of

time. Daily measurements of the fastest mile are presented in the monthly Local Climatological Data (LCD) summaries.<sup>10</sup> The duration of the fastest mile, typically about 2 min (for a fastest mile of 30 mph), matches well with the half life of the erosion process, which ranges between 1 and 4 min. It should be noted, however, that peak winds can significantly exceed the daily fastest mile.

The wind speed profile in the surface boundary layer is found to follow a logarithmic distribution:

$$u(z) = \frac{u^*}{0.4} \ln \frac{z}{z_0} \quad (z > z_0) \quad (3-2)$$

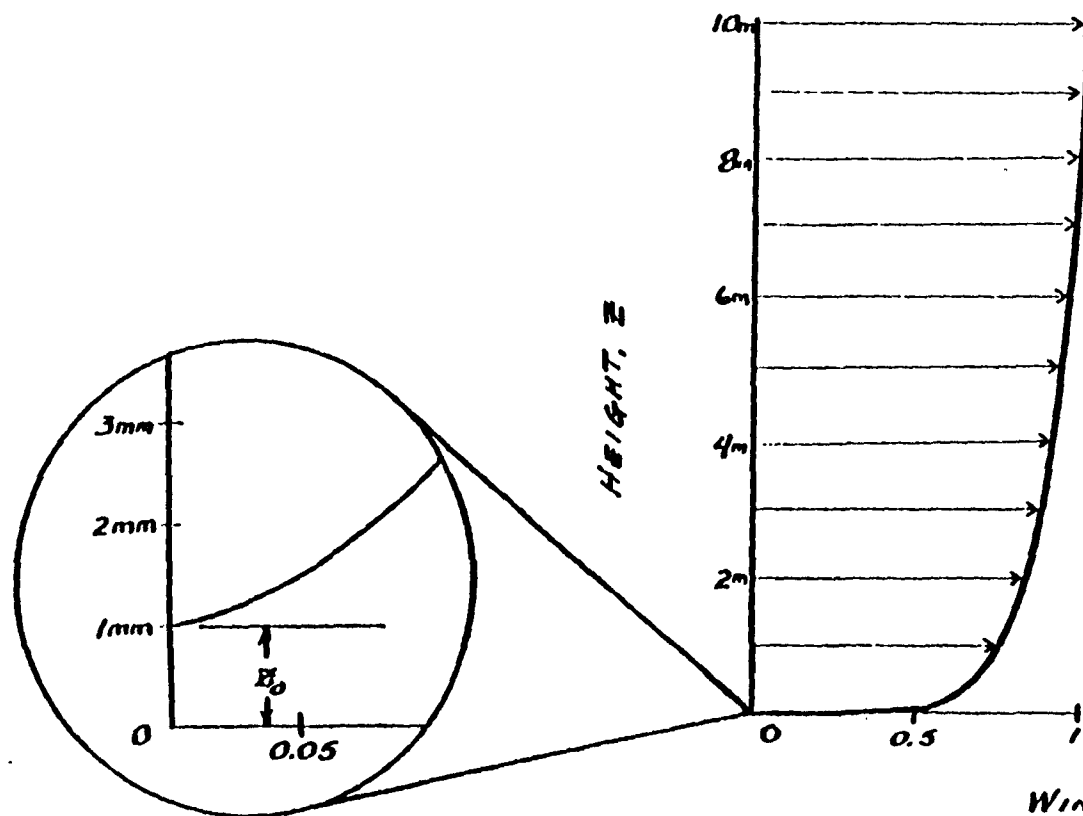
where:  $u$  = wind speed, cm/s  
 $u^*$  = friction velocity, cm/s  
 $z$  = height above test surface, cm  
 $z_0$  = roughness height, cm  
0.4 = von Karman's constant, dimensionless

The friction velocity ( $u^*$ ) is a measure of wind shear stress on the erodible surface, as determined from the slope of the logarithmic velocity profile. The roughness height ( $z_0$ ) is a measure of the roughness of the exposed surface as determined from the y-intercept of the velocity profile, i.e., the height at which the wind speed is zero. These parameters are illustrated in Figure 3-2 for a roughness height of 0.1 cm. The roughness height ( $z_0$ ) is needed to convert the friction velocity to the equivalent wind speed at the typical weather station sensor height of 7 to 10 m above the surface.

Emissions generated by wind erosion are also dependent on the frequency of disturbance of the erodible surface because each time that a surface is disturbed, its erosion potential is restored. A disturbance is defined as an action which results in the exposure of fresh surface material. On a storage pile, this would occur whenever aggregate material is either added to or removed from the old surface. A disturbance of an exposed area may also result from the turning of surface material to a depth exceeding the size of the largest pieces of material present.

3-8

# ARITHMETIC REPRESENTATION



# SEMI-LOGARITHMIC REPRESENTATION

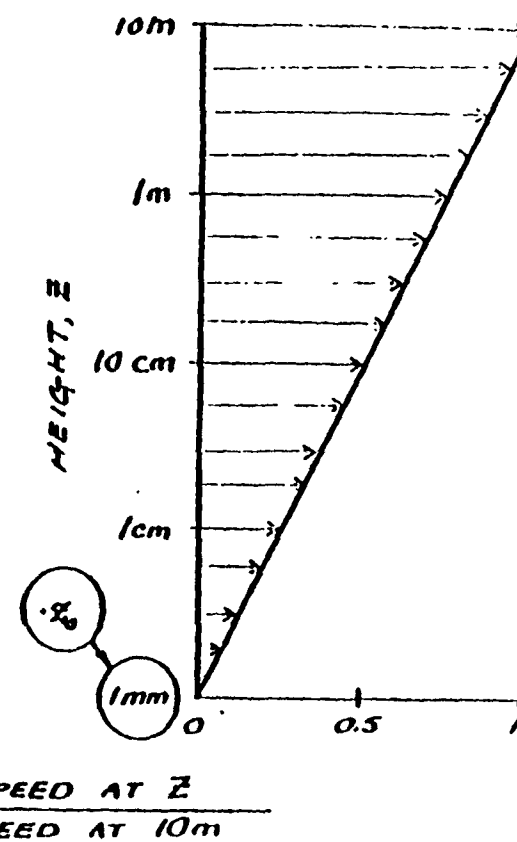


Figure 3-2. Illustration of logarithmic velocity profile.

3.2.2.2 Predictive Emission Factor Equation<sup>11</sup>. The emission factor for wind-generated particulate emissions from mixtures of erodible and nonerodible surface material subject to disturbance may be expressed in units of g/m<sup>2</sup>-yr as follows:

$$\text{Emission factor} = k \sum_{i=1}^N P_i \quad (3-3)$$

where:  $k$  = particle size multiplier  
 $N$  = number of disturbances per year  
 $P_i$  = erosion potential corresponding to the observed (or probable) fastest mile of wind for the  $i$ -th period between disturbances, g/m<sup>2</sup>

The particle size multiplier ( $k$ ) for Equation 3-3 varies with aerodynamic particle size, as follows:

Aerodynamic Particle Size Multipliers for Equation 3-3

$\frac{<30 \text{ } \mu\text{m}}{1.0}$	$\frac{<15 \text{ } \mu\text{m}}{0.6}$	$\frac{<10 \text{ } \mu\text{m}}{0.5}$	$\frac{<2.5 \text{ } \mu\text{m}}{0.2}$
--	--	--	---

This distribution of particle size within the  $< 30 \text{ } \mu\text{m}$  fraction is comparable to the distributions reported for other fugitive dust sources where wind speed is a factor. This is illustrated, for example, in the distributions for batch and continuous drop operations encompassing a number of test aggregate materials (see AP-42 Section 11.2.3).

In calculating emission factors, each area of an erodible surface that is subject to a different frequency of disturbance should be treated separately. For a surface disturbed daily,  $N = 365/\text{yr}$ , and for a surface disturbance once every 6 mo,  $N = 2/\text{yr}$ .



The erosion potential function for a dry, exposed surface has the following form:

$$\begin{aligned} P &= 58 (u^* - u_t^*)^2 + 25 (u^* - u_t^*) \\ P &= 0 \text{ for } u^* \leq u_t^* \end{aligned} \quad (3-4)$$

where:  $u^*$  = friction velocity (m/s)

$u_t^*$  = threshold friction velocity (m/s)

Table 3-2 presents the erosion potential function in matrix form. Because of the nonlinear form of the erosion potential function, each erosion event must be treated separately.

Equations 3-3 and 3-4 apply only to dry, exposed materials with limited erosion potential. The resulting calculation is valid only for a time period as long or longer than the period between disturbances.

For uncrusted surfaces, the threshold friction velocity is best estimated from the dry aggregate structure of the soil. A simple hand sieving test of surface soil (adapted from a laboratory procedure published by W. S. Chepil<sup>12</sup>) can be used to determine the mode of the surface aggregate size distribution by inspection of relative sieve catch amounts. This procedure is specified in Section 4.2.1. The threshold friction velocity for erosion can be determined from the mode of the aggregate size distribution, following a relationship derived by Gillette,<sup>13</sup> as shown in Figure 3-3.

Threshold friction velocities for several surface types have been determined by field measurements with a portable wind tunnel.<sup>13-16</sup> These values are presented in Tables 3-3 and 3-4 for industrial aggregates and Arizona sites. Figure 3-4 depicts these data graphically.

The fastest mile of wind for the periods between disturbances may be obtained from the monthly LCD summaries for the nearest reporting weather station that is representative of the site in question.<sup>10</sup> These summaries report actual fastest mile values for each day of a given month.

TABLE 3-2. EROSION POTENTIAL FUNCTION

$u_{*c}$ m/s	$u_t^* =$	$P \text{ (g/m}^2\text{)}$											
		0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4
0.2		0	0	0	0	0	0	0	0	0	0	0	0
0.4		7	0	0	0	0	0	0	0	0	0	0	0
0.6		19	7	0	0	0	0	0	0	0	0	0	0
0.8		36	19	7	0	0	0	0	0	0	0	0	0
1.0		57	36	19	7	0	0	0	0	0	0	0	0
1.2		83	57	36	19	7	0	0	0	0	0	0	0
1.4		114	83	57	36	19	7	0	0	0	0	0	0
1.6		149	114	83	57	36	19	7	0	0	0	0	0
1.8		188	149	114	83	57	36	19	7	0	0	0	0
2.0		233	188	149	114	83	57	36	19	7	0	0	0
2.2		282	233	188	149	114	83	57	36	19	7	0	0
2.4		336	282	233	188	149	114	83	57	36	19	7	0
2.6		394	336	282	233	188	149	114	83	57	36	19	7
2.8		457	394	336	282	233	188	149	114	83	57	36	19
3.0		525	457	394	336	282	233	188	149	114	83	57	36

TABLE 3-3. THRESHOLD FRICTION VELOCITIES--INDUSTRIAL AGGREGATES

Material	Threshold friction velocity, m/s	Roughness height, cm	Threshold wind velocity at 10 m (m/s)		Ref.
			$z_0 =$ actual	$z_0 =$ 0.5 cm	
Overburden <sup>a</sup>	1.02	0.3	21	19	9
Scoria (roadbed material) <sup>a</sup>	1.33	0.3	27	25	9
Ground coal <sup>a</sup> (surrounding coal pile)	0.55	0.01	16	10	9
Uncrusted coal pile <sup>a</sup>	1.12	0.3	23	21	9
Scraper tracks on coal pile <sup>a,b</sup>	0.62	0.06	15	12	9
Fine coal dust on concrete pad <sup>c</sup>	0.54	0.2	11	10	15

<sup>a</sup>Western surface coal mine.<sup>b</sup>Lightly crusted.<sup>c</sup>Eastern power plant.TABLE 3-4. THRESHOLD FRICTION VELOCITIES--ARIZONA SITES<sup>16</sup>

Location	Threshold friction velocity (m/s)	Roughness height (cm)	Threshold wind velocity at 10 m (m/s)
Mesa - Agricultural site	0.57	0.0331	16
Glendale - Construction site	0.53	0.0301	15
Maricopa - Agricultural site	0.58	0.1255	14
Yuma - Disturbed desert	0.32	0.0731	8
Yuma - Agricultural site	0.58	0.0224	17
Algodones - Dune flats	0.62	0.0166	18
Yuma - Scrub desert	0.39	0.0163	11
Santa Cruz River, Tucson	0.18	0.0204	5
Tucson - Construction site	0.25	0.0181	7
Ajo - Mine tailings	0.23	0.0176	7
Hayden - Mine tailings	0.17	0.0141	5
Salt River, Mesa	0.22	0.0100	7
Casa Grande - Abandoned agricultural land	0.25	0.0067	8

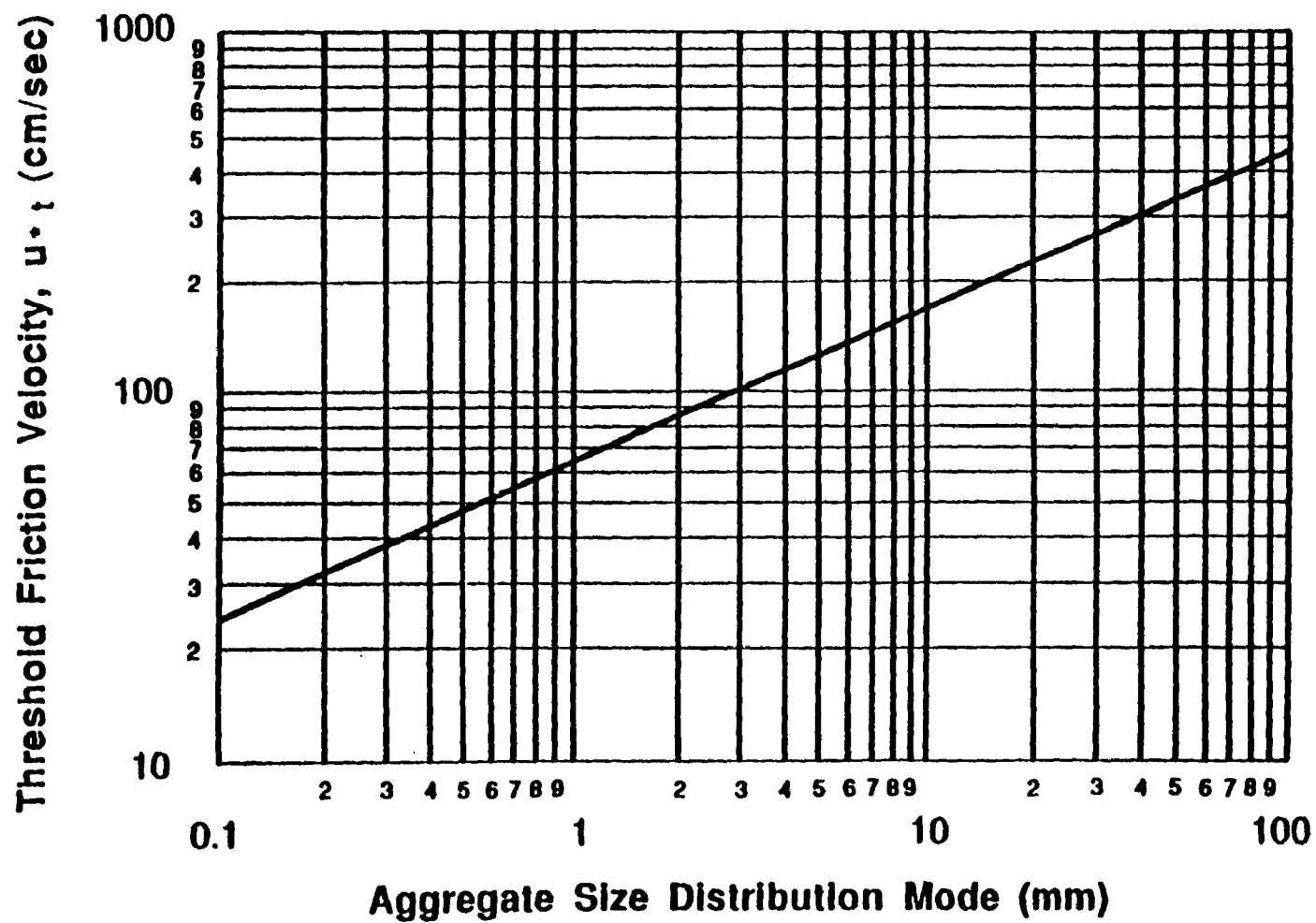


Figure 3-3. Relationship of threshold friction velocity to size distribution mode.

For narrowly sized, finely divided materials only

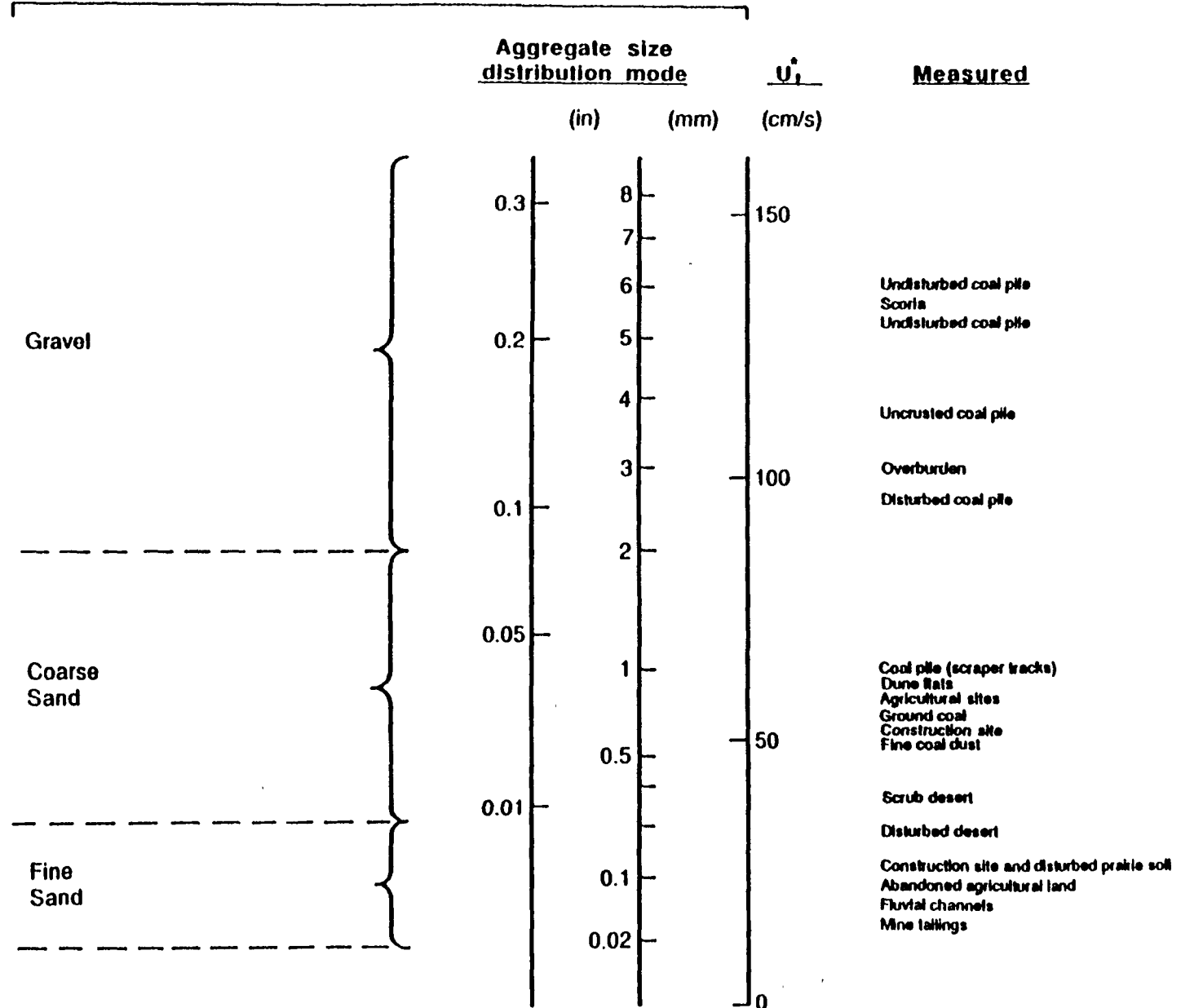


Figure 3-4. Scale of threshold friction velocities.



Because the erosion potential is a highly nonlinear function of the fastest mile, mean values of the fastest mile are inappropriate. The anemometer heights of reporting weather stations are found in Reference 17, and should be corrected to a 10 m reference height using Equation 3-2.

To convert the fastest mile of wind ( $u^+$ ) from a reference anemometer height of 10 m to the equivalent friction velocity ( $u^*$ ), the logarithmic wind speed profile may be used to yield the following equation:

$$u^* = 0.053 u_{10}^+ \quad (3-5)$$

where:  $u^*$  = friction velocity (m/s)  
 $u_{10}^+$  = fastest mile of reference anemometer for period between disturbances (m/s)

This assumes a typical roughness height of 0.5 cm for open terrain. Equation 3-5 is restricted to large relatively flat piles or exposed areas with little penetration into the surface wind layer.

If the pile significantly penetrates the surface wind layer (i.e., with a height-to-base ratio exceeding 0.2), it is necessary to divide the pile area into subareas representing different degrees of exposure to wind. The results of physical modeling show that the frontal face of an elevated pile is exposed to wind speeds of the same order as the approach wind speed at the top of the pile.

For two representative pile shapes (conical and oval with flat-top, 37 degree side slope), the ratios of surface wind speed ( $u_s$ ) to approach wind speed ( $u_r$ ) have been derived from wind tunnel studies.<sup>14</sup> The results are shown in Figure 3-5 corresponding to an actual pile-height of 11 m, a reference (upwind) anemometer height of 10 m, and a pile surface roughness height ( $z_0$ ) of 0.5 cm. The measured surface winds correspond to a height of 25 cm above the surface. The area fraction within each contour pair is specified in Table 3-5.

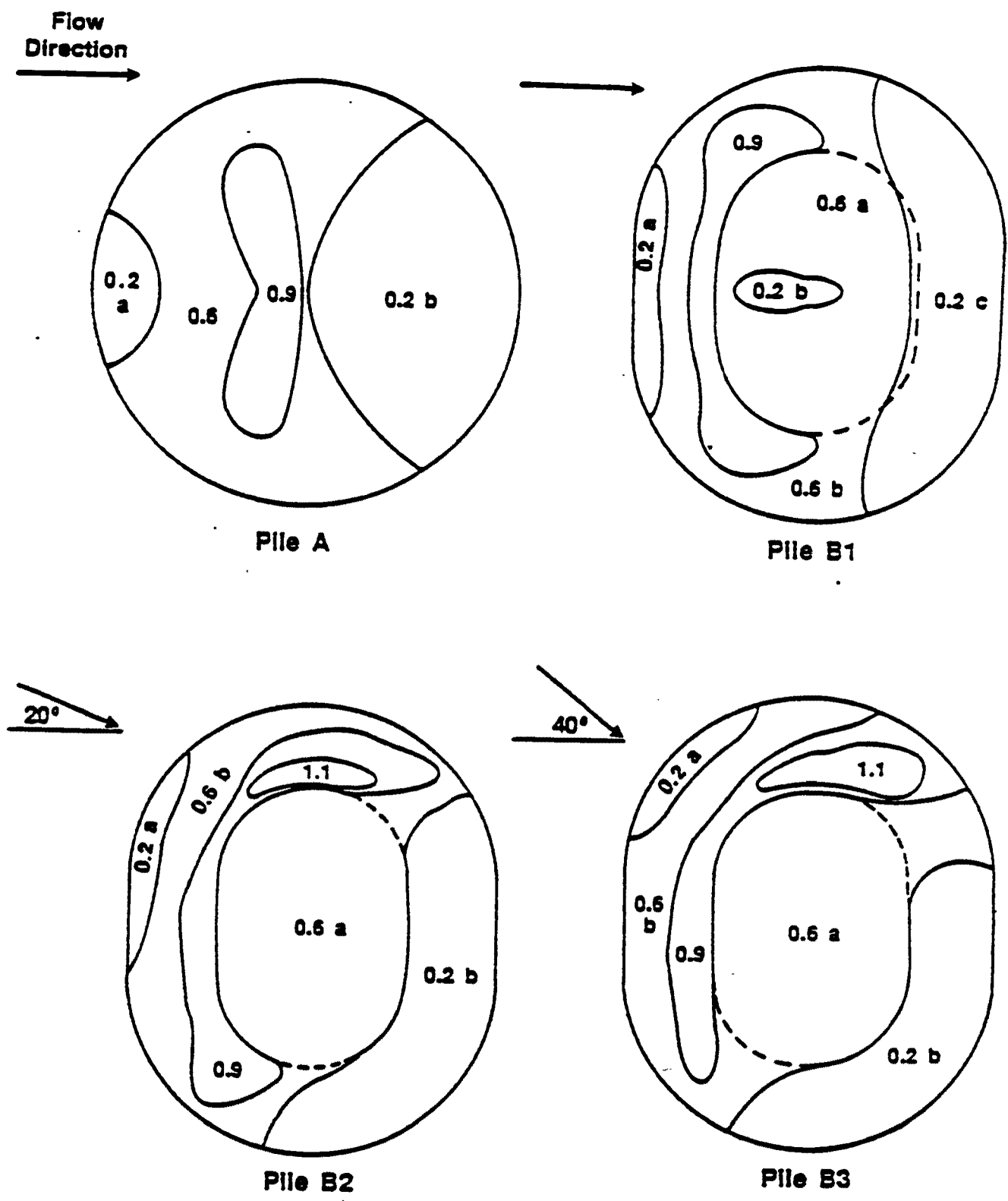


Figure 3-5. Contours of normalized surface wind speeds,  $u_s/u_r$ .

TABLE 3-5. SUBAREA DISTRIBUTION FOR REGIMES OF  $u_s/u_r$ 

Pile subarea	Percent of pile surface area (Figure 3-3)			
	Pile A	Pile B1	Pile B2	Pile B3
0.2a	5	5	3	3
0.2b	35	2	28	25
0.2c	-	29	-	-
0.6a	48	26	29	28
0.6b	-	24	22	26
0.9	12	14	15	14
1.1	-	-	3	4

The profiles of  $u_s/u_r$  in Figure 3-5 can be used to estimate the surface friction velocity distribution around similarly shaped piles, using the following procedure:

1. Correct the fastest mile value ( $u^+$ ) for the period of interest from the anemometer height ( $z$ ) to a reference height of 10 m ( $u_{10}^+$ ) using a variation of Equation 3-2, as follows:

$$u_{10}^+ = u^+ \frac{\ln(10/0.005)}{\ln(z/0.005)} \quad (3-6)$$

where a typical roughness height of 0.5 cm (0.005 m) has been assumed. If a site specific roughness height is available, it should be used.

2. Use the appropriate part of Figure 3-5 based on the pile shape and orientation to the fastest mile of wind, to obtain the corresponding surface wind speed distribution ( $u_s^+$ ), i.e.,

$$u_s^+ = \left(\frac{u_s}{u_r}\right) u_{10}^+ \quad (3-7)$$

3. For any subarea of the pile surface having a narrow range of surface wind speed, use a variation of Equation 4-2 to calculate the equivalent friction velocity ( $u^*$ ), as follows:

$$u^* = \frac{0.4 u_s^+}{\ln \frac{25}{0.5}} = 0.10 u_s^+ \quad (3-8)$$



From this point on, the procedure is identical to that used for a flat pile, as described above.

Implementation of the above procedure is carried out in the following steps:

1. Determine threshold friction velocity for erodible material of interest (see Tables 3-3 and 3-4 or use Figure 3-3 to determine the mode of the aggregate size distribution).
2. Divide the exposed surface area into subareas of constant frequency of disturbance ( $N$ ).
3. Tabulate fastest mile values ( $u^+$ ) for each frequency of disturbance and correct them to 10 m ( $u_{10}^+$ ) using Equation 3-6.
4. Convert fastest mile values ( $u_{10}^+$ ) to equivalent friction velocities ( $u^*$ ), taking into account (a) the uniform wind exposure of nonelevated surfaces, using Equation 3-5, or (b) the nonuniform wind exposure of elevated surfaces (piles), using Equations 3-7 and 3-8.
5. For elevated surfaces (piles), subdivide areas of constant  $N$  into subareas of constant  $u^*$  (i.e., within the isopleth values of  $u_s/u_r$  in Figure 3-5 and Table 3-5) and determine the size of each subarea.
6. Treating each subarea (of constant  $N$  and  $u^*$ ) as a separate source, calculate the erosion potential ( $P_i$ ) for each period between disturbances using Equation 3-4 and the emission factor using Equation 3-3.
7. Multiply the resulting emission factor for each subarea by the size of the subarea, and add the emission contributions of all subareas. Note that the highest 24-h emissions would be expected to occur on the windiest day of the year. Maximum emissions are calculated assuming a single event with the highest fastest mile value for the annual period.

The recommended emission factor equation presented above assumes that all of the erosion potential corresponding to the fastest mile of wind is lost during the period between disturbances. Because the fastest mile event typically lasts only about 2 min, which corresponds roughly to the half-life for the decay of actual erosion potential, it could be

argued that the emission factor overestimates particulate emissions. However, there are other aspects of the wind erosion process which offset this apparent conservatism:

1. The fastest mile event contains peak winds which substantially exceed the mean value for the event.
2. Whenever the fastest mile event occurs, there are usually a number of periods of slightly lower mean wind speed which contain peak gusts of the same order as the fastest mile wind speed.

Of greater concern is the likelihood of overprediction of wind erosion emissions in the case of surfaces disturbed infrequently in comparison to the rate of crust formation.

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16. ABSTRACT  <p>This report is a compendium of models (equations) for estimating air emissions from Superfund sites undergoing remediation. These models predict emission rates of volatile organic compounds (VOC's) and particulate matter (PM) from both area and point sources. The following remedial processes are covered: air stripping, soil vapor extraction, thermal desorption, thermal destruction (incineration), excavation, dredging, solidification/stabilization, and bioremediation. Emission estimation methods are also presented for landfills, lagoons, and spills/leaks/open waste pits.</p> <p>The models contained in this compendium will not accurately predict emissions for all possible scenarios. Where uncertainty exists, these models and the default inputs have been designed to overpredict emissions.</p>		
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